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Irradiation processing of ready-to-eat meats

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CHAPTER 1. GENERAL INTRODUCTION

The convenience provided by ready-to-eat (RTE) meat products has made them one of the most popular meat items in the United States. This increase in popularity and the recent foodborne outbreaks associated with these products have alerted the scientific community. *Listeria monocytogenes* has been one of the pathogens connected with foodborne outbreaks caused by RTE meats. Since this pathogen can be found throughout the environment it represents a potential source of post lethality microbial contamination. Once the finished product is contaminated, the organism has little trouble growing in most RTE products at refrigeration temperatures even with salt and nitrite present. In addition, *L. monocytogenes* has very little competition for nutrients from other organisms because thermal processing, vacuum packaging, addition of salt and nitrite and refrigerated conditions inhibit most competitors. Furthermore, unlike fresh, uncooked meats that normally receive thermal processing to ensure microbiological safety, RTE meats are often consumed without any heat treatments prior to consumption. This pathogen survives many of the food safety interventions commonly used to preserve RTE meat products if post lethality contamination occurs. Hence, RTE products make an excellent growing media for *L. monocytogenes* making its control very difficult in this product category.

The U.S. Department of Agriculture released a directive in 2003 that requires that processors who produce post-lethality exposed RTE meats take further actions to prevent contamination of RTE meats with *L. monocytogenes*. One of the requirements to comply with the regulation is the use of a post-lethality treatment that had demonstrated to be effective eliminating microorganisms on meat products. Irradiation has proved to be effective eliminating and/or reducing the population o f pathogenic as well as non-pathogenic

bacteria from prepackaged foods. Hence, this technology will enable the food industry to eliminate bacterial contamination from food after processing.

The effectiveness of irradiation to eliminate microbial contamination in meat products may be limited by the changes it causes in the chemical environment of meat products. Quality attributes such as color, odor, and flavor may be altered as a result of these chemical changes. Consequently, the quality attributes of irradiated RTE meats may be objectionable to the consumer. Therefore, manipulation of the chemical environment of the meat must be studied to find ways to minimize the changes in quality attributes of irradiated meat products and bring the quality attributes to an acceptable level for the consumers

The overall objectives of this research were to investigate the effects of irradiation processing on the quality characteristics of meat products prepared with pork, beef, chicken, and turkey that fall into the RTE product category. The effect of pH and irradiation processing on the production of volatiles and sensory properties of ham were also studied. Quality attributes tested included color, volatile production, lipid oxidation, odor/aroma, off-aroma, flavor and off-flavor.

Dissertation Organization

This dissertation is organized into six chapters which include an introduction, literature review, three complete manuscripts and general conclusions. The work presented in the first two manuscripts was completed in cooperation with Dr. Terry A. Houser, who received his Ph.D. in Meat Science from Iowa State University in 2004. Dr. Houser and I shared ideas and duties in designing the projects, manufacturing or acquiring the products to be tested, testing the products, analyzing the data, and interpreting the results. The

manuscripts were prepared using the *Journal of Food Science Style Guide*. The first manuscript "Effects of irradiation at 1.6 kGy on quality characteristics of commercially produced ham and pork frankfurters over extended storage" was co-authored with Dr. Terry A. Houser, Dr. Joseph Sebranek, Dr. Joseph Cordray, Dr. Bryon Wiegand, Dr. Dong Ahn and Dr. Eun Lee. The second manuscript "The effects of irradiation on color, odor, flavor and production of volatiles of ready-to-eat beef, chicken and turkey" was co-authored with Dr. Joseph Cordray, Dr. Terry A. Houser, Dr. Joseph Sebranek, Dr. Dong Ahn and Dr. Eun Lee. The third manuscript "The effects of pH and irradiation processing on the production of volatiles and sensory properties of ham" was co-authored with Dr. Joseph C. Cordray, Dr. Terry A. Houser, Dr. Joseph G. Sebranek, Dr. Dong Ahn, Dr. Aubrey F. Mendonca and Dr. Dermot J. Hayes.

CHAPTER 2. LITERATURE REVIEW

Meat and Meat Flavors

The flavor of raw meat is no more than a blood-like taste with little or no aroma (Bender and Balance 1961). Meat flavor development is a thermally derived process that combines precursors of meat flavor present in raw meat. The two major categories of meat flavor precursors are the water soluble components and the lipid components. Upon heating, volatile compounds produced during the Maillard reaction and the thermal degradation of lipids dictate the aroma attributes and most of the flavor characteristics of cooked meat (Mottram 1991).

Precursors of meat flavor

Despite the enormous effort of researchers to isolate and characterize meat flavor compounds, this desirable characteristic of meat can not be attributed to a specific compound or group of compounds (Mottram 1991). Studies have identified low molecular weight, water-soluble compounds and lipids as the two main categories of meat flavor precursors. However, the role of high molecular weight components and their contribution in the development of flavor and flavor compounds must be considered (Shahidi 1994). The water-soluble components include free sugars, sugar phosphates, free amino acids, peptides, nucleotides and other nitrogen-containing compounds such as thiamine and cysteine (Mottram 1991). The amino acids and peptides contribute to sweet or bitter flavors. The acid flavor comes from the lactic, inosinic, succinic, orthophosphoric and other acids present in the meat. Sugars provide the sweet flavor and the sodium salts impart the salty flavors (Moody 1983). The 5'-ribonucleotides, glutamic acid and monosodium glutamate are believed to act as meat flavor enhancers. Studies have suggested that the lean portion of

meat provides a basic meaty flavor to all species and the lipid portion is responsible for the flavor differences among species (Mottram 1991). The proportion of unsaturated to saturated fatty acids in meat may contribute to the distinct flavor characteristics of cooked meat from different species (Noleau and Toulemonde 1987).

Volatile compounds in meat

Hydrocarbons

Hydrocarbons are produced via thermal oxidative decomposition of fatty acids. n-Alkanes and n-alkenes are formed from lipid hydroperoxides and they constitute the major aliphatic hydrocarbons in meat (Forss 1972). Only a few alicyclic hydrocarbons including terpenes such as limonine have been found in lean meat (Mottam 1991). Hydrocarbons represent the largest class of cooked meat volatiles. However, reviews of the literature indicate that their contribution to meat flavor is relatively minor (Shahidi and others 1986)

Alcohols

Meat contains both unsaturated and saturated alcohols. The majority of the alcohols are produced via oxidative decomposition of fat (Shahidi and others 1986). Saturated alcohols are present in high concentration in meat; however it is believed that they play a minor role in meat flavor due to their high threshold values. The low threshold value of unsaturated alcohols, on the other hand, provides an indication that they may contribute to the meat flavors derived form the lipid components (Mottran 1991). Peterson and Shang (1982) reported that high concentrations of 1-penten-3-ol in stew meat resulted in a greasy, ethereal odor. 1-octen-3-ol, which has been associated with a mushroom-like odor, was also found at high levels in stew meat.

Aldehydes

Aldehydes can be produced via thermal degradation, oxidative decomposition or Strecker degradation of amino acids (Mottram 1991). This class of volatiles is considered a major contributor of meat flavor and odor. The low threshold values of some aldehydes make them potential flavor compounds at very low concentrations (Shahidi and others 1991). Mabrouk (1976) reported that further reactions of dicarbonyls, dienals, and trienals resulted in the production of flavor notes in specific proportions for different species. Mottram (1991) stated that unsaturated aldehydes may play an important role in species-characteristic flavors.

Ketones

The production of ketones from lipids may contribute to the fatty, oily and metallic notes of meat. Chicken contains more unsaturated ketones than red meats (Mottram 1991). Alicyclic ketones such as cyclopentanones and cyclohexanones have been identified in beef (MacLeod and Ames 1986). The authors suggested that these ketones contribute to the increased meatiness found in flavor isolates.

Carboxylic acids

The free fatty acids in meat are derived from triglycerides and phospholipids in the lipid portion of the meat. Therefore, the amount and proportion of free fatty acids in meat differ between species (Mottram 1991). Large numbers of carboxylic acids have been identified in mutton compared to those identified in beef, pork and poultry meat (Shahidi and others 1986). Medium-chain fatty acids are more volatile than long-chain fatty acids. For instance, it is believed that medium-chain fatty acids contribute more to the flavor differences between species (Mottram 1991).

Lactones

Lactones have been associated with different odor notes in meat. Forss (1972) reported oily, buttery, fatty and fruity odor notes form lactones. Lactones have been detected in beef fat and pork liver, however no lactones have been identified in chicken (Shahidi and others 1986).

Furans

Furans are not considered a major contributor of meat aroma. However, they form part of the overall broiled or roasted odor notes of meat (Shahidi and others 1986). Oxygenated furans may act as intermediates to other compounds including sulfur-containing compounds that impart meat flavors. More than 62 furans have been identified in meat with the majority undergoing substitution in the 2-position. They usually carry other functional groups such as carbonyls, alcohols, thiol and sulfide groups (Mottram 1991).

Nitrogen compounds

Some nitrogen-containing volatiles include pyrroles, pyridines. pyrazines, and pyrimidines. Pyrroles and pyrrolidienes may be produced via pyrolysis of amino acids (Mottram 1991). Pyrazines arise from Maillard reactions (Shahidi and others 1986). These nitrogen compounds are associated with roasted meat flavors.

Sulfur compounds

Sulfur compounds can be produced by the Maillard reaction of reducing sugars with sulfur-containing amino acids (Whitfield and others 1988). Hydrogen sulfide has been identified as the basic sulfur compound involved in the development of meaty flavor in all species (Shahidi and others 1986). It is produced during the Streker degradation of cysteine and its main role is to act as a reactant in the production of flavor compounds (Mattram 1991). Sulfur-containing volatiles have been reported to have many different aroma

characteristics associated with meat (Boelens and others 1974; Wasserman 1979; Mottram 1998). Although sulfur-containing compounds are major contributors of meat flavor, some of these compounds impart flavor notes that are not desirable (Boelens and others 1974). Sulfides and polysulfides have strong, objectionable odors (Mottram 1991). Therefore, the amount and type of sulfur-containing compounds present could determine the acceptability of meat flavors.

The flavor of meat

The characteristic flavor of meat develops during cooking. The cooking methods used to prepare meat provide a wide variation of temperature ranges and cooking conditions. Medium-rare roast beef may only reach an internal temperature of 50°C. Poultry frankfurters may be cooked to internal temperatures higher than 71°C. Pork ribs cooked on a grill may undergo localized dehydration and reach very high surface temperatures (Mottram 1991). Hence, the wide range of flavor sensations among the products mentioned above should not be surprising.

Wasserman (1979) reported that temperature and moisture control the physical and chemical changes that meat compounds experience during cooking. Pyrolysis of amino acids and peptides and the degradation of sugars occur mainly in the surface of products (Mottram 1991). Decarboxylation and deamination of peptides and amino acids may occur at temperatures higher than 125°C. These reactions lead to the formation of aldehydes, hydrocarbons, nitriles and amines. Surface dehydration needs to take place in order to reach temperatures above the boiling point of water (Mottram 1991). Although the concentration of sugars in fresh meat is low, studies have reported the degradation of reducing sugars to yield furanones. Hydroxymethylfuranones, produced during aqueous degradation of sugars,

react with hydrogen sulfide to form compounds that have been associated with meat aromas (van den Ouweland and Peer 1975).

Hornstein and Crowe (1960) reported that cold-water-extracted proteins from lean beef and pork samples were responsible for the development of meaty aroma when the meat batter was heated to 100°C. However, protein alone cannot account for the entire meat aroma. Batzer and others (1960) reported that both protein and carbohydrate were necessary to produce meat flavor in ground beef heated to 77°C. The reaction of protein with carbohydrate is known as the Maillard reaction. The Maillard reaction is considered one of the main mechanisms for the formation of compounds that contribute to the development of meat flavor. In contrast to the pyrolysis of amino acids and sugar caramelization, the Maillard reaction does not requires high temperatures (Mottram 1991). Factors such as temperature, time, moisture content, pH and the concentration and nature of the reactants affect the reaction rate (Bailey 1998). The formation of flavor compounds generally occurs at temperatures associated with cooking (Wasserman 1979).

The Maillard reaction starts by the condensation of the carbonyl group of a reducing sugar with an amino compound, which yields a glycosylamine (Hodge 1953; Mottram 1998). The thermally unstable compounds produced via the Maillard reaction undergo dehydration and deamination to produce furans similar to those obtained via sugar caramelization and a number of other degradation products (Tressl and others 1979). Maillard products are involved in further reactions with compounds such as amines, amino acids, and hydrogen sulfide that result in the formation of many important classes of flavor compounds. Pyrazines, oxazoles, thiophenes, thiazoles and other heterocyclic sulfur compounds are

examples of the classes of flavor compounds formed when Millard products interact with other compounds present in food (Mottram 1991).

Volatiles from the lipid fraction of meat are produced via thermal oxidative lipid degradation. The thermal oxidation reactions follow the same general route that occurs during the development of rancidity (Mottram 1991). However, changes in the mechanism yield different concentrations of compounds that result in different flavor profiles between the two systems (Grosch 1982). Thermal oxidative degradation occurs as fatty acids are broken down to form alcohols, aldehydes and other products from secondary reactions (Mottram and others 1982; Mottram and Edwards 1983). The oxidation of saturated fatty acids is a mechanism unique to heated systems (Grosch 1982), hence these compounds may also contribute to variations in aroma profiles between thermal oxidation and rancidity (Mottram 1991). In heated systems, the concentration of hydroperoxides remains relatively low because they are extremely heat liable. The different proportion of radical intermediates available during cooking compared to the proportion available at lower temperatures may lead to variations in the compounds formed and their concentration in the product (Mottram 1991).

The interaction of lipid fractions with other heat-induced compounds needs to be considered in the formation of flavor during cooking. Studies have shown that the triglyceride fraction of lipid does not contribute as much as the phospholipids fraction due to increased amounts of unsaturated fatty acids found in the phospholipids. Farmer and Mottram (1992) compared heated beef triglyceride with beef phospholipids for aroma and volatile production in a heated (60°C) system. These researchers described the aroma of the beef triglyceride as fatty, greasy, with no species-specific aroma whereas the beef

phospholipids had a chicken, meaty and beef-dripping aroma. The authors reported higher levels of unsaturated fatty acids for the beef phospholipids compared to the beef triglyceride.

In a similar study, Mottram and Edwards (1983) demonstrated the need for phospholipids in attaining meaty aroma by extracting both triglycerides and phospholipids prior to heating of the meat mixture. These researchers reported an increase in volatile alkylpyrazines for the defatted mixtures as evidenced by gas chromatography, which resulted in increased nutty flavors and decreased meaty aromas. It was suggested that the presence of lipid in the meat system inhibits the formation of pyrazines formed during the Maillard reaction. Whitfield and others (1988) studied the role of phospholipids and their effect upon Maillard products from selected amino acids and ribose. In this experiment glycine, cysteine, and lysine were heated at 140°C in the presence of ribose and lecithin. It was determined by gas chromatography-mass spectrometry that when the amino acids were heated with ribose furans, pyrazines, pyridines and pyrroles were formed. In addition, when cysteine was heated with ribose, additional thiophenes, thiazoles and sulphur-containing heterocyclics that were not present in the glycine or lysine volatile components were formed. When lecithin was added to these mixtures, additional heterocyclic compounds were formed in addition to aliphatic aldehydes, alcohols and ketones. Additionally, when lecithin was heated with cysteine and ribose, a decrease in thiophenes and thiazoles were observed. These observations led to the conclusion that lecithin could inhibit the production of sulfur-containing volatiles in the Maillard reaction of cysteine and ribose. This effect was not universal for all volatiles as an increase in some alkylfurans, pentylpyridines and alkylthiophenes were reported.

The flavor of cured meat

The unique multifunctional properties of nitrite play an important role in the flavor development of cured meats. Its antioxidant properties (Pearson and others 1977) and ability to prevent warmed over flavor (Rubin and Shahidi 1988) have been associated with the development of cured meat flavor. Researchers have attributed the difference in flavor between nitrite-cured meats and uncured cooked meats to the suppression of lipid oxidation products. Cross and Ziegler (1965) studied the volatile composition of cured and uncured ham. These researchers found that a much greater amount of hexanal and pentanal production occurred in the uncured ham samples using gas chromatography. This increased carbonyl content was thought to come from oxidation of fatty acids in the uncured meat. In addition, the authors reported the presence of characteristic cured ham aroma in both the cured ham and uncured ham after the samples were passed through 2-4 dinitrophenylhydrazine solutions to remove the carbonyls. It was concluded that the cured ham aroma was not from the carbonyl fraction but from precursors other than triglycerides and was the characteristic meaty aroma found in all cured and uncured meat products. These findings have been confirmed more recently by Ramarathnam and others (1991) who reported fewer volatile constituents in cured cooked ham compared to uncured cooked ham using gas chromatography. The authors reported that the production of carbonyl compounds was the main difference in the volatile constituents. The study demonstrated that greater amounts of carbonyls were present in the uncured ham samples compared to the cured samples. The hexanal content was much greater in the uncured ham samples (12.7 mg/kg) compared to the cured ham samples (0.03 mg/kg). Other carbonyls were also reported to be higher in the uncured ham samples compared to the cured ham samples.

Lipid oxidation during storage

The oxidation of lipids comprises three phases; initiation, propagation, and termination (Figure 3). The initiation step is triggered by reactive species (initiators) capable of removing a hydrogen atom from a methylene group in lipid molecules. Some of these reactive oxygen species include hydroxyl radicals, superoxide anions, hydrogen peroxide, hydroperoxyl radicals and iron-oxygen complexes. The propagation step eventually follows with the formation of a fatty acyl radical (L•) which reacts with oxygen, forming a peroxy radical (LOO•). It is during this step when a chain reaction is set off, further oxidizing the unsaturated fatty acids present in the food (Morissey and others 1998). The propagation step is completed when the LOO•s react with each other to form non-reactive products (Min and Ahn 2005).

Initiation

$$LH + Initiator^{\bullet} \rightarrow L^{\bullet} + InitiatorH$$

Propagation

$$L^{\bullet} + O2 \rightarrow LOO^{\bullet}$$

$$LOO^{\bullet} + LH \rightarrow LOOH + L^{\bullet}$$

Termination

$$L^{\bullet} + L^{\bullet} \rightarrow RR$$

$$L^{\bullet} + LOO^{\bullet} \rightarrow LOOL$$

$$LOO^{\bullet} + LOO^{\bullet} \rightarrow LOOL + O2$$

Figure 3. Mechanism for Lipid Oxidation (Min and Ahn 2005)

Lipid oxidation is one of the main factors limiting the quality and acceptability of meats and meat products (Morrissey and others 1998). The acceptability of the product depends on the extent to which oxidative rancidity has occurred (Gray 1978). Muscle foods have inherent antioxidant properties which can be classified as lipid, cytosolic and enzymic antioxidant systems. The level of protection provided by these three systems is dependent on animal species, muscle type, and diet. The primary mode of action of the lipid and cytosolic antioxidant systems involves scavenging free radicals and chelating free metal ions. The amounts of lipid and cytosolic antioxidant activity are dependent upon diet and anatomical location as a result of muscle fiber type. The enzymic antioxidant system catalyzes the conversion of highly reactant oxidation species to less reactive products.

During further processing, antioxidants such as nitrites, ascorbates and polyphosphates can be added to the meat to control lipid oxidation. Nitrite inhibits lipid oxidation by stabilizing lipid membranes, chelating free iron, and stabilizing the iron-heme complex. Ascorbate functions as a regenerator of α-tocopherol, which can scavenge free radicals when incorporated into muscle. The polyphosphates act as chelators of proxidant metals that would otherwise serve as lipid oxidation catalysts (Kanner 1994; Decker and Mei 1996; Morrissey and others 1998).

The addition of nitrite to meats lessens lipid oxidation (Shahidi and others 1991). Killday (1988) proposed that nitrite and its products have the ability to hinder lipid oxidation by stabilizing the iron heme complex and preventing heme iron from reacting with unsaturated fatty acids. The stabilization of the iron heme complex also prevents the reaction of iron with lipid hydroperoxides (ROOH) during the propagation step to form peroxyl radicals (ROO•) and alkoxyl radicals (RO•) that readily react with oxygen (Morrissey and

others 1998). Another proposed mechanism for nitrite and its products to prevent lipid oxidation is the stabilization of double bonds at which free radicals can attack (Erduran and Hotchkiss 1995).

A common method used to measure lipid oxidation in meat systems is the 2-thiobarbituric acid (TBA) test or more recently referred to as the 2-thiobarbituric acid reactive substances (TBARS) test. Tarladgis and others (1960) developed the TBA test to measure the milligrams of malonaldehyde per 1000 g of product in the test sample. Studies have shown a correlation coefficient of 0.89 between the TBA values and the sensory taste panel. Furthermore, a threshold range of 0.5 to 1.0 has been reported for detection of off-odor in fresh ground pork ham (Tarladgis and others 1960).

Lipid oxidation products can also be measured by volatile analysis via gas chromatography. Ahn and others (1998) irradiated (0 and 4.5 kGy) fresh pork patties packaged in aerobic and anaerobic environments, which were subsequently stored and cooked. The same researchers determined the extent of lipid oxidation in irradiated (0 and 4.5 kGy) pork patties by TBARS and volatile analysis via gas chromatography. A correlation coefficient between TBARS and total volatiles was reported to be 0.93. Additionally, a 0.94 correlation coefficient was reported between volatile hexanal content and TBARS. Another study by Ahn and others (1999) confirmed the ability of gas chromatography to measure lipid oxidation products in irradiated (0, 2.5 and 4.5 kGy), cooked, ground pork packaged in anaerobic and aerobic atmospheres. The TBARS values were significantly ($P<0.0001$) correlated to the amount of total volatile detected in the samples. The authors proposed the used of total volatile production and hexanal production as indicators of lipid oxidation in meat products.

Irradiation

Ionizing radiation refers to a form of radiation that has enough energy to produce positive and negative charges to kill live organisms. Today, this technology has many commercial applications in medical, pharmaceutical, and food operations (Thayer and others 1996). Gamma rays, X rays, and accelerated electrons are the three types of ionizing radiation that can be applied to food (Olson 1998). Gamma rays are obtained from radioactive isotopes such as cobalt-60 or cesium-137 as a result of their natural decay over time (Renwick and Hansen 1996). The energy level emitted by these isotopes has been reported to be about 1 to 2 MeV (Olson 1995). Linear accelerators or Van de Graaff generators can be used to accelerate electrons to energy levels of 10 MeV or more in order to be used for the application of irradiation treatments. Accelerated electrons are transformed into x-rays by making them collide with a film of heavy metal. Today, gamma rays from cobalt-60 and accelerated electrons are the sources of ionizing radiation available for commercial food operations (Olson 1995).

Gamma irradiation is characterized by its ability to penetrate deep into products (Renwick and Hansen 1996). Gamma rays can penetrate 30 cm of water with a radiation energy between 0.15 and 4 MeV (Rosenthal 1992). Gamma irradiation from cobalt-60 is frequently used to irradiate substantial amounts of products. The utilization of this technology often requires processing large quantities of product for a long period of time to obtain a maximum throughput from this type of system (Renwick and Hansen 1996). X-rays, as gamma rays, are also highly penetrating. However, the most remarkable difference between the two systems is that x-rays contain a wide range of wavelengths in comparison with the uniform wavelengths emitted by gamma sources (Rosenthal 1992).

Also, the production of x-rays leads to an enormous loss of electron beam energy (Renwick and Hansen 1996).

In order to make use of all the power produced by the e-beam machine, the accelerated electrons have to be applied directly to the food. Unfortunately, these accelerated electrons do not penetrate very deep into the product (Renwick and Hansen 1996). Electron beam irradiation is frequently used for the treatment of surfaces or thin products (Rosenthal 1992). Accelerated electrons can penetrate up to 8.9 cm at 10 MeV in products that have the density of water when using double-sided irradiation (Olson 1995). Electron beam (EB) irradiation seems to be more feasible to treat small amounts of product quickly. This type of technology may allow processors to utilize ionizing radiation for in-line treatments optimizing the utilization of the equipment (Renwick and Hansen 1996).

Regulatory agencies have limited the energy levels that can be emitted by irradiation sources that will be used for the treatment of foods to prevent the production of artificial radioactive substances in the products (Rosenthal 1992). Gamma ray and x-rays are limited to a maximum energy of 5 MeV, and accelerated electrons produced by machines are limited to a maximum of 10 MeV (Thayer and others 1996).

It is important to determine the irradiation dose that is to be applied to the food during the irradiation process (Olson 1995). The effect of ionizing radiation in the treated product depends on the absorbed dose (Woods and Pikaev 1994). The Gray (Gy) is the unit used to measure radiation doses in the International System of Units. One Gray is equivalent to 1 joule of energy absorbed per kilogram of food (Olson 1995). The irradiation doses applied to food are classified as low dose, lower than 1 kGy, medium dose, 1 to 10 kGy, and high dose, 10 to 50 kGy (Woods and Pikaev 1994). Dosimeters, such as alanine pellets, are

recommended to measure the irradiation dose in food because they cover a wide range of doses (10 Gy to 50 kGy) and do not contaminate the product being treated (McLaughlin and others 1989).

Investigators have not found a unique radiolytic product produced by irradiation. The chemical products detected after the irradiation treatment of food are the same formed in products exposed to heat, light, and oxygen (Woods and Pikaev 1994). Irradiation has been applied for many years to a variety of medical and pharmaceutical products including intravenous administration sets, operating room towels, syringes and needles, etc. Irradiation also has been used for the treatment of some consumer products such as cosmetics, baby bottle nipples, and contact lens cleaning solutions (Thayer and others 1996). This technology has a wide variety of applications in the food industry including inhibition of sprouting in vegetables, delay of ripening in fruits, killing insects, pathogenic bacteria and parasites, and extension of shelf life among others (Rosenthal 1992). In the United States, the utilization of irradiation treatments has been approved for wheat and wheat flour, white potatoes, herbs, spices and vegetables seasonings, fruit and vegetables, dehydrated enzymes, animal and pet food, poultry, and trichina inactivation in pork (Thayer and others 1996). More recently, the use of ionizing radiation treatment was approved for refrigerated and frozen uncooked red meats. (USDA, FSIS 1999)

Irradiation of fresh meat

The muscles of healthy animals are sterile. However, their exposure to the environment during the slaughter process provides the microbial contamination frequently present on the surface of the carcasses. Further processing, such as carcass fabrication, spreads bacterial contamination to all exposed meat surfaces (Shay and others 1988). Food

borne pathogens such *as Staphylococcus aureus, Escherichia coli O157:H7, and Listeria monocytogenes* may be present in meat and poultry products. Radiation treatments (1.5-10 kGy) can be used to reduce and/or eliminate pathogenic as well as non-pathogenic bacteria (Thayer and others 1996). However, irradiation treatments produce changes in color, flavor, and odor that may reduce the acceptability of irradiated meats (Shay and others 1988). Vacuum packaging and low temperature storage can be used to reduce the undesirable changes produced by ionizing irradiation (Rosenthal 1992; Olson 1995).

Pathogens such as *Salmonella, Campylobacter and Staphylococcus aureus* did not survive 3.0 kGy irradiation dose in fresh, vacuum-packaged pork loins stored at 2 to 4°C (Lebepe and others 1990). Low dose (0.75 to 0.90 kGy) electron beam irradiation reduced approximately 2 logs of L. monocytogenes in pork chops. Furthermore, the pathogen was not detected by direct plating or Most Probable Number method when a medium dose (1.8 to 2.0 kGy) was applied to this product (Fu and others 1995). Andrews and others (1995) also found that 10^3 colony-forming units (CFU) of L. monocytogenes per milliliter of tryptic soy broth did not survive a 2.0 kGy dose of gamma irradiation. Niemand and others (1981) observed a drastic shift from gram-negative to gram-positive types of microorganism in irradiated (2.0 kGy), vacuum packaged beef cuts. Ehioba and others (1988) found similar results in vacuum packaged, ground pork irradiated with a dose of 1.0 kGy and stored at 5°C. An irradiation dose of 3.0 kGy was found to significantly ($P < 0.05$) reduce mesophilic, anaerobic, and facultative-anaerobic microorganism in vacuum packaged pork loins (Lebepe and others 1990).

Irradiation of meat product might be limited by several factors that affect the product's flavor, color, and odor (Shay and others 1988). Free radicals produced during

irradiation treatments and their reaction with food may lead to changes in the color, flavor, and odor in the product being treated. The production of these free radicals has been associated with the reaction of ionizing radiation and water (Proctor and others 1952). These radicals can yield lipid radicals via free radical reactions and/or hydroperoxides in the presence of oxygen (Thakur and Singh 1994). Ionizing radiation treatments have been reported to promote the formation of peroxides when oxygen is around and/or within the food (Lee and others 1996). These peroxides subsequently deteriorate into a variety of compounds such as alkanes, alkenes, aldehydes, and alcohols during further reactions (Patterson and Stevenson 1995). The extent of the changes produced by ionizing irradiation may vary depending on the food being treated, the dose being applied, and the processing techniques being used (Proctor and others 1952).

Investigators agree that the presence of oxygen during the irradiation process increases color deterioration in fresh meat (Urbain 1986; Shay and others 1988; Lambert and others 1992; Lefebvre and others 1994). This type of discoloration has been attributed to the production of brown metmyoglobin and the destruction of the porphyrin ring that yields to formation of a green color (Groninger and others 1956). Modified atmosphere packaging (MAP), such as vacuum or carbon dioxide (CO_2), resulted in the production of a more desirable color in irradiated (1.75 kGy) pork chops (Grant and Patterson 1991). Fresh meat treated under modified atmosphere showed a conversion of the brown metmyoglobin to the desirable pink color of oxymyoglobin (Groninger and others 1956).

Irradiation treatments (0.0-10.5 kGy) did not affect the CIE L* (lightness) values of fresh, vacuum packed beef steaks, boneless pork chops, or turkey breasts (Nanke and others 1998). On the contrary, Lambert and others (1992) reported that the L* values of irradiated

(0.0-1.0 kGy) pork were higher than the L* values of the control. Zhao and others (1996) reported that irradiated fresh pork generally has higher L* values than non-irradiated pork. Lebepe and others (1990) reported that Hunter a* (redness) values were higher in irradiated, vacuum packaged pork loins than non-irradiated loins. Nanke and others (1998) reported a significant increase in a* values as the irradiation dose was increased from 0.0 kGy to 10.5 kGy in vacuum packed pork and from 0.0 kGy to 4.5 kGy in vacuum packed turkey. Lynch and others (1991) reported that irradiated (2.5 kGy), vacuum packaged, raw turkey fillets had a more desirable pink color than the control when evaluated by a sensory panel. An increase in the b* (yellowness) values of irradiated pork was observed as the irradiation dose was increased from 0.0 kGy to 4.5 kGy. The same changes in b* values were observed in irradiated turkey when the doses were increased from 0.0 kGy up to 7.5 kGy (Nanke and others 1998). Lambert and others (1992) observed similar changes in b* values in irradiated (0.5-1.0 kGy) pork loins packaged in a 100% nitrogen (N_2) modified atmosphere. On the other hand, Fu and others (1995) did not find differences in b* values in irradiated (0.75-1.98 kGy) vacuum packaged pork chops.

Some of the undesirable color changes in meat products and the initial stages of lipid oxidation are interrelated. The greater proportion of unsaturated to saturated fatty acids found in pork and turkey and their susceptibility to lipid oxidation may explain the relationship between lipid oxidation and color oxidation in these species (Akamittath and others 1990). The oxidation of fat has been found to be accelerated by gamma irradiation (Lea and others 1960). Groninger and others (1956) reported that the peroxide values of irradiated ground pork increased as the irradiation doses were increased. Lefebvre and others (1994) observed similar results in ground beef. Zhao and others (1996) reported that the

TBARS values of irradiated (1.0 kGy), vacuum packaged pork chops were significantly higher ($P < 0.05$) than the control. Mattison and others (1986) and Lambert and others (1992) reported that irradiation (1.0 kGy) did not affect the TBARS values of vacuum packed pork loins. An irradiation dose of 2.5 kGy did not increase the TBARS values of vacuum packaged, raw turkey breast patties stored at 4°C (Ahn and others 1997).

Significant changes in meat flavor and aroma have been reported even at irradiation doses as low as 2.0 kGy (Shay and others 1988). Off-odors produced during the irradiation treatment of fresh meats might be associated with the possible production of volatile sulfur compounds from glutathione and proteins containing sulfhydryl groups (Batzer and Doty 1955). Ahn and others (2000) hypothesized that the off-odors produced in irradiated meats are the result of the radiolytic breakdown of sulfur-containing amino acids. Dimethyltrisulphide was reported to be the main sulfur containing compound present in raw chicken meat treated with a medium dose (2.5 kGy) of ionizing irradiation (Patterson and Stevenson 1995). Grant and Patterson (1991) reported that the odor of irradiated pork changed from a "burnt" odor to a "dairy" odor during storage due to the proliferation of lactic acid bacteria in a modified atmosphere package. Lynch and others (1991) reported that turkey fillets treated with irradiation (2.5 kGy) developed an objectionable odor that increased after 21 days of storage according to a trained sensory panel. An irradiation "threshold" dose for organoleptic changes in fresh pork and turkey irradiated at 5 to 10°C has been reported to be about 1.75 kGy (Urbain 1986; Grant and Patterson 1991), and 1.50 kGy (Urbain 1986), respectively.

Irradiation of processed meat

The heat treatments typically used by the meat industry in the production of ready-to-eat meat products provide the bacterial reduction necessary to ensure the wholesomeness of these products. However, pathogens such as *Listeria monocytogenes* had been detected in ready-to-eat meat products at retail stores. Pathogenic as well as non-pathogenic bacteria can be reintroduced to cooked products during the slicing and packaging processes (Wang and Muriana 1994). Studies on high-dose irradiation treatments demonstrated the efficacy of ionizing irradiation to eliminate bacterial contamination in processed meats (Anellis and others 1972; Baburt and others 1987; Crawford and Ruff 1996). The United States Army successfully developed irradiated canned products such as ham, chicken, and turkey (WHO 1994). However, other studies focused on radappertization (sterilization by irradiation) of canned meats reported significant changes in the sensory characteristics of irradiated meat products (Groninger and others 1956; Shults and others 1977a, Shults and others 1977b). Today, the incidence of foodborne outbreaks associated with processed meats have stimulated the scientific community to look at low and medium doses of ionizing radiation as a possible tool for the elimination of pathogenic bacteria from pre-packaged product such as ready-to-eat meats (Olson 1995).

Patterson (1989) reported that *L. monocytogenes* can be eliminated from poultry mince meat using medium (2.5-7.0 kGy) irradiation doses. Fu and others (1995) reported that a medium dose (1.8-2.0 kGy) of electron beam irradiation produced a substantial reduction of *L. monocytogenes* in cured hams, but some cells were able to recover after the temperature of the product was increased from 7 to 25°C to simulate product mishandling.

Thayer and others (1998) observed a higher decimal reduction values for *L. monocytogenes* in pre-cooked irradiated (3.0 kGy) turkey nuggets than in raw, irradiated turkey nuggets.

Gamma radiation (32 kGy) was found to decrease the cured color intensity of ham (Kamarei and others 1981). Shuts and others (1977a) reported that as the irradiation dose increased from 2.5 to 4.5 megarad (25-45 kGy), the discoloration rating increased in corned beef briskets. Groninger and others (1956) observed a significant reduction in the color of irradiated cured hams after a dose of 2.0 megarep (20 kGy) of gamma radiation was applied to the product. However, a medium dose (1.8-2.0 kGy) of ionizing irradiation did not affect the color of vacuum packaged ham stored at 2-4°C (Fu and others 1995).

The lipid oxidation process in cured meats has been reported to be lower than in cooked meats as long as the meat pigment is in the ferrous state (Love and Pearson 1971). Upon storage, the color of cured meat is converted to metmyoglobin and the lipid oxidation is accelerated (Younathan and Watts 1959). Terrell and others (1981) observed an increase in the TBARS values of irradiated frankfurters when the irradiation doses were increased from 0.0 to 3.2 megarad (0.0-32 kGy). Ahn and others (1998) reported that the TBARS values of irradiated (2.5 kGy) and then cooked turkey breast patties were not affected by the irradiation treatment. Similar results were found by Shults and others (1977a) in irradiated (25-45 kGy) corned beef briskets. Shults and others (1977b) observed lower TBARS values in irradiated (30-60 kGy) canned pork rolls when compared with the control.

Changes in sensory perceptions of irradiated (5.0 kGy) hams were found to be ($P < 0.01$) unacceptable by a group of volunteer families in a consumer acceptability test in Denmark. The participants detected ($P < 0.01$) odors and flavors not normally associated with ham in the irradiated samples (Hansen 1966). A non-characteristic odor was detected in

sliced ham and bologna irradiated at doses between 2 x 10^5 to 2 x 10^6 rep (2.0-20 kGy) in an aerobic environment. The odor of the ham did not change upon storage, however, the bologna developed a rancid odor after 7 days of storage (Erdman and Watts 1957). Irradiated (32 kGy) frankfurters were found to have a strong off-flavor and a significant reduction ($P < 0.05$) in their overall palatability when compared with the control (Terrell and others 1981). The odor of irradiated and then cooked chicken thighs was found to be affected after a dose of 2.0 kGy was applied to the product. The same study revealed that irradiation treatments up to 3.0 kGy have no detrimental effects on the odor of chicken breast cooked up to 85°C (Heath and others 1990).

The concentration of aldehydes such as propanal, pentanal, and hexanal have been reported to be higher in irradiated (2.5 kGy), cooked turkey meat stored for 7 days at 4°C (Ahn and others 1998). Also, an increase in the amount of carbonyl compounds was observed in pre-cooked, irradiated (18.6-27.9 kGy), canned pork chops and veal shoulder clods stored at 2°C. The same study revealed that the cooking process increases the concentration of carbonyls and hydrogen sulfides followed by a further increase as a result of the irradiation treatment (Pearson and others 1959).

Consumer Acceptance of Irradiated Meats

Although food irradiation research has been made available to the public, consumers still have very limited knowledge about irradiation processing (Bruhn 1995). Studies have shown the willingness of consumers to pay more for a food product guaranteed to be free of *Salmonella* or *Trichinella spiralis* (Shin and others 1992). However, researchers found that when consumers are presented with both positive and negative information about irradiation processing, the negative information dominates the willingness of the consumer to pay to

control *Trichinella* in pork reducing the number of bids for the irradiated pork (Hayes and others 2002).

Resurreccion and others (1995) reported that 32.6% of 446 consumers surveyed believed irradiated foods contain radioactivity. Participants (48.7%) were not certain about whether or not irradiated foods contained radioactivity. Hayes and others (2002) reported that food safety ratings for irradiated pork decreased compared to the typical product when negative information was made available to consumers. The same study also demonstrated that presenting both negative and positive information about irradiation processing have the same effect as that of providing only negative information.

However, if consumers are exposed to accurate educational information, it has been reported that purchasing of irradiated products would increase. Hashim and others (1995) reported that the percent of participants willing to purchase irradiated poultry products increased from 59.5% to 83.3% for boneless skinless chicken breasts and 61.9% to 85.7% for chicken thighs by using an educational slide program. Positive information increases the consumer's perception that irradiated pork is safe (Hayes and others 2002). Eustice (2003) estimated that 6,500 supermarkets in the US carry at least some irradiated meat products and between 2000-3000 restaurants are serving irradiated meat products.

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CHAPTER 3. EFFECTS OF IRRADIATION AT 1.6 kGy ON QUALITY CHARACTERISTICS OF COMMERCIALLY PRODUCED HAM AND PORK FRANKFURTERS OVER EXTENDED STORAGE

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Abstract

Commercially produced sliced, ham and all-pork frankfurters were obtained from a national meat processor and irradiated at 1.6 kGy. The samples were evaluated for color, lipid oxidation, odor, flavor, and the production of volatiles over an 8-week storage period. Irradiation processing did not affect color values for the ham or frankfurters. Lipid oxidation as measured by 2-thiobarbituric acid reactive substances (TBARS) did not increase for either the ham or frankfurters. Irradiation processing increased off-odor scores for the ham but not for frankfurters. Off-flavor scores were not significantly different for ham but were higher in frankfurters due to irradiation processing. Dimethyl disulfide content increased as a result of irradiation in both the ham and frankfurters but decreased over the 8-week storage period. Irradiation processing resulted in the formation of new volatile compounds in the ham samples including heptane, trans-1-butyl-2-methylcyclopropanone, 2-octene and toluene, which were not present in non-irradiated ham. Irradiation treatment resulted in the formation of 2-butanone in the frankfurters, which was not present in the non-irradiated frankfurters. Most volatile compounds that were affected by irradiation processing for both the ham and frankfurters increased when compared to non-irradiated controls. Although color and lipid oxidation (TBARS) did not seem to be affected by irradiation processing at 1.6 kGy, changes

in odor, flavor and the production of volatiles are of concern if irradiation is to be used to control microbial growth in ready-to-eat pork products.

Keywords: ham, pork frankfurters, color, lipid oxidation, volatiles.

Introduction

On June 6, 2003, the United States Department of Agriculture (USDA) Food Safety and Inspection Service (FSIS) issued new regulations to control contamination of post-lethality exposed ready-to-eat (RTE) meat products with *Listeria monocytogenes* (USDA 2003). The regulations encourage use of a post-lethality treatment to reduce or eliminate microorganisms for compliance. Irradiation has been shown to be effective in reducing or eliminating microorganisms including *Listeria monocytogenes* in meat products (Fu and others 1995; Gürsel and Gürakan 1997). However, while irradiation is approved by the USDA for fresh/frozen red meats and poultry, it is not currently approved for RTE meats.

It is clear that irradiation would be an effective post-lethality treatment for cured RTE meats to control *Listeria monocytogenes* but changes in quality characteristics of these products have been reported (Houser and others 2003; Zhu and others 2003). Sensory characteristics are the properties that seem to be impacted the greatest by irradiation processing and therefore are of greatest interest. Terrell and others (1981a; 1981b) reported increasing off-odor scores for frankfurters as irradiation dose increased from 0 to 8.0 kGy. Houser and others (2003) reported that off-odor scores from a trained sensory panel were significantly ($P<0.05$) higher for sliced boneless RTE ham irradiated at 4.5 kGy compared to non-irradiated controls at day 0. However, scores were not significantly ($P>0.05$) different after 30 days of storage. On the other hand, Fu and others (1995) reported no evidence of a

difference ($P>0.05$) in off-odor between irradiated (1.8 kGy) and non-irradiated cured ham slices. This disagreement may be due to the different irradiation doses that were used.

Irradiation has also been reported to increase the amount of off-flavors present in RTE meats in addition to off-odor. Zhu and others (2003) reported a dose-dependent increase in sulfur odor/flavor scores by a trained sensory panel as a result of increasing irradiation dose from 0-2 kGy in RTE turkey ham. The increased sulfur odors/flavors detected by the panelists were confirmed by measurement of volatile compounds using gas chromatography. For example, the amount of dimethyl disulfide increased significantly ($P<0.05$) as irradiation dose increased. Furthermore, carbon disulfide was not present in the non-irradiated samples but was present in irradiated samples at both doses used. Additionally, increased off-flavors have been reported when increased doses of irradiation have been used. Terrell and others (1981a; 1981b; 1982) reported significantly higher off-flavor levels when pork/beef frankfurters were irradiated at 8 and 32 kGy compared with non-irradiated controls.

Although RTE meats in the US are manufactured with many different species of meat raw materials, pork is one of the most popular. Sliced, boneless ham and all-pork frankfurters are very common in the US market and would be excellent candidates for irradiation processing due to their uniform size and shape. In addition, RTE meats in general are expected to have a shelf life in excess of 60 days. Therefore, the objectives of this research were to determine the effect of irradiation processing on quality characteristics including lipid oxidation, production of volatiles, color, odor and flavor of commercially-available sliced, boneless, cured ham and all-pork frankfurters over an extended storage period.

Materials and Methods

Four separate batches of sliced ham and smoked pork frankfurters were obtained from a national meat processor. The ingredients for the ham included ham muscles, water, potassium lactate, carrageenan, dextrose, salt, sodium phosphate, sodium erythorbate and sodium nitrite. The ingredients for the frankfurters included pork, water, salt, flavorings, hydrolyzed milk protein, sorbitol, autolyzed yeast, sodium phosphate, ascorbic acid, sodium nitrite and paprika. The sliced ham and pork frankfurter samples were sent to the Iowa State University Meat Laboratory (Ames, IA., U.S.A.) under refrigerated conditions directly from the processing facilities where they were manufactured. After the products arrived at the Iowa State Meat Laboratory, they were taken out of their original packages, placed into barrier bags (Cryovac B540, Cryovac Sealed Air Corp., Duncan, SC., U.S.A.) and vacuum-packaged (Multivac Model A6800 vacuum packager, Multivac Inc., Kansas City, MO., U.S.A.). The packaging film had an O_2 transmission rate of 3-6 cc/m^2/24 hr at 1 atm, 4.4°C and 0% RH, and a water vapor transmission rate of 0.5-0.6 g/645 cm^2/24 hr and 100% RH. The resulting ham packages contained 10 slices per package and the packages of frankfurters contained 8 frankfurters per package.

After repackaging, the samples were randomly assigned to 0 and 1.6 kGy treatments and were sent under refrigerated conditions to SureBeam Corporation (Glendale Heights, IL., U.S.A.). Upon arrival at SureBeam Corp., the products were maintained at 2-4°C for between 1-3 days until irradiation processing. Samples were irradiated by an electron beam accelerator (SureBeam Corp. Glendale Heights, IL., U.S.A.) to an average absorbed dose of 1.6 kGy with a maximum/minimum dose ratio of 1.21. After irradiation treatment, samples were returned under refrigerated conditions to the Iowa State Meat Laboratory and were

stored in cardboard boxes at 2-4°C until the products were analyzed. Purge loss, color measurements, lipid oxidation, odor evaluation, flavor evaluation and volatile analysis were conducted for all treatments after 0, 2, 4, 6 and 8 weeks of storage. Week 0 samples were measured within 2-5 days after irradiation treatment and subsequent measurements were done at 14-day intervals.

Proximate composition was determined for the ham and frankfurters including crude fat (ether extract method, AOAC 1990a), moisture (air oven drying method, AOAC 1990b) and crude protein (combustion method, AOAC 1993).

Purge loss % was calculated as product weight loss divided by the initial weight, multiplied by 100.

The pH of the ham and frankfurters was determined by blending the samples with distilled water in a 1:9 ratio, then measuring the pH with a pH/ion meter (Accumet 925: Fisher Scientific, Fair Lawn, NJ., U.S.A.) equipped with an electrode (Accumet Flat Surface Epoxy Body Ag/AgCl Combination Electrode Model 13-620-289, Fisher Scientific, Fair Lawn, NJ., U.S.A.) according to the method of Sebranek and others (2001).

Color measurements were conducted using a Hunterlab Labscan colorimeter (Hunter Associated Laboratories Inc., Reston, VA., U.S.A.). The Hunterlab Labscan colorimeter was standardized using the same packaging material as used on the samples, placed over the white standard tile. Values for the white standard tile were X=81.72, Y=86.80 and Z=91.46. Illuminate A, 10° standard observer with a 2.54 cm viewing area and 3.05 cm port size was used to analyze the ham samples and a 0.64 cm viewing area and 1.02 cm port size was used to analyze the external and internal color of the frankfurter samples. Commission International d'Eclairage (CIE) L* (lightness), a* (redness) and b* (yellowness)

measurements were taken at 4 randomly selected areas on the samples and the resulting average was used in data analysis (Hunt and others 1991). All of the measurements were taken while products were maintained in vacuum packaged conditions with the exception of the internal color of the frankfurters. Internal color of frankfurters was measured after slicing the frankfurters in half lengthwise and immediately measuring the internal color.

Lipid oxidation was measured by the modified 2-thiobarbituric acid reactive substances (TBARS) test as described for cured meats (Zipser and Watts 1962). TBARS values were reported as mg of malonaldehyde equivalents/kg of meat sample.

Ham and frankfurter samples used for odor analysis were taken out of the package immediately after opening, cut into pieces, then placed into plastic dishes with covers. Samples used for flavor analysis were presented to the panelists separately from the samples used in the odor analysis. The sliced ham samples were evaluated by the panelists without reheating, which would be characteristic for this product. The frankfurters were heated on an electric range top in boiling water and were subsequently served warm to the panelists, which would be characteristic of consumer preparation for this product. Trained panelists (10-12), made up of Iowa State University students and staff, were used for each session. Panelists were trained to distinguish between samples irradiated at 0 and 8 kGy. For training, non-irradiated samples were used to represent no off-odor/off-flavor and 8 kGy samples were used to represent distinct off-odor/off-flavor. This permitted panelists to distinguish irradiation odors/flavors from normal odors/flavors. Panelists evaluated experimental samples for odor using a line scale with graduations from 0-150 mm, where 0 represented no off-odor and 150 represented intense off-odor. Additionally, panelists evaluated

experimental samples for flavor using a line scale with graduations from 0-150 mm, where 0 represented no off-flavor and 150 represented intense off-flavor.

Production of volatiles was determined using a Solatek 72 Multimatrix-Vial Autosampler/Sample Concentrator 3100 (Tekmar-Dohrmann, Cincinnati, OH., U.S.A.) connected to a gas chromatograph/mass spectrometer (GC/MS; Model 6890/5973, Hewlett-Packard Co., Wilmington, DE., U.S.A.) according to the method of Ahn and others (2001). The ham and frankfurter samples (3 g) were placed in a 40-mL sample vial, flushed with helium gas (40 psi) for 3 s and then capped airtight with a Teflon*fluorocarbon resin/silicone septum (I-Chem Co., New Castle, DE., U.S.A.). The maximum waiting time for a sample in a loading tray (4°C) was less than 2 h to minimize oxidative changes before analysis. The meat samples were purged with helium (40 mL/min) for 14 min at 40°C. Volatiles were trapped using a Tenax/charcoal/silica column (Tekmar-Dohrmann, Cincinnati, OH., U.S.A.) and desorbed for 2 min at 225°C, focused in a cryofocusing module (-80°C) and then thermally desorbed into a column for 60 s at 225°C. A HP-624 column (7.5 m, 0.25 mm i.d., 1.4 μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.), a HP-1 column (60 m, 0.25 mm i.d., 0.25μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.) and a HP-Wax column (7.5 m, 0.25 mm i.d., 0.25 μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.) were connected using zero dead-volume column connectors (J &W Scientific, Folsom, CA, U.S.A.). A ramped oven temperature was used to improve volatile separation. The initial oven temperature of 0°C was held for 1.5 min. After that, the oven temperature was increased to 15°C at 2.5°C per min, increased to 45°C at 5°C per min, increased to 110°C at 20°C per min, then increased to 210°C at 10°C per min and held for 2.25 min at that temperature. Constant column pressure at 22.5 psi was maintained. The ionization

potential of the MS was 70 eV and the scan range was 19.1 to 350 m/z. The identification of volatiles was achieved using the Wiley library (Hewlett-Packard Co., Wilmington, DE., U.S.A.). The area of each peak was integrated using ChemStation™ software (Hewlett-Packard Co., Wilmington, DE., U.S.A.) and the total peak area (total ion counts x 10^4) was reported as an indicator of volatiles generated from the samples.

The experimental design was a split plot with blocks at the main plot level. The main plot consisted of 4 blocks (4 separate batches of ham/frankfurters) and 2 irradiation doses (0 and 1.6 kGy). The split plot contained 5 sampling periods (0, 2, 4, 6 and 8 weeks) and combined with the main plots resulted in 40 observations. Statistical analysis was performed for all measurements using the Statistical Analysis System (1999-2001, Version 8.2, SAS Institute Inc., Cary, NC., U.S.A.) Mixed Model procedure (Proc Mixed). The main effects were irradiation treatment and replication. The random effect was replication*irradiation treatment. Least squares means were used to determine level of significance at $P<0.05$ after adjustment for all pair-wise comparisons using the Tukey-Kramer procedure.

Results and Discussion

Proximate composition was 2.8% fat, 74.7% moisture and 16.3% protein for the ham and 24.2% fat, 57.2% moisture and 12.4% protein for the frankfurters. There were no significant ($P>0.05$) differences in % purge loss due to irradiation treatment or storage time for the ham or frankfurters. In addition, there were no significant ($P>0.05$) differences in pH due to irradiation treatment for the ham or frankfurters.

There were no significant effects ($P>0.05$) of irradiation treatment on CIE L*, a* and b* values for the ham or frankfurters. These results agree with Fu and others (1995) who

reported no differences in color scores for irradiated (1.8 kGy) ham compared with non-irradiated controls. However, Houser and others (2003) reported significantly lower L* values for irradiated (4.5 kGy) cooked ham compared with non-irradiated controls. This difference could be due to the differences in irradiation doses in the two studies. A dose-dependent change in L* values has been reported by Zhu and others (2003) who reported a significant decrease in lightness values in irradiated turkey ham as irradiation dose increased from 0 to 2 kGy.

Lipid oxidation as measured by TBARS analysis showed no significant differences ($P>0.05$) due to irradiation treatment or storage time for either the ham or frankfurters. This agrees with Houser and others (2003) who reported that TBARS values of irradiated (4.5 kGy) ham was not practically different than non-irradiated control. Because sodium nitrite was used in both product formulations and has been shown to be an effective anti-oxidant, these results were expected (Shahidi and others 1991). If irradiation (1.6 kGy) affected TBARS values in pork products, the frankfurters would be more likely to show this difference due to their relatively high fat content in comparison to the ham. However, when higher doses of irradiation are used, it is possible that lipid oxidation could increase. Terrell and others (1981a) reported a dose-dependent increase in TBARS values for irradiated (0, 8 and 32 kGy) pork/beef frankfurters.

Off-odor scores were significantly ($P<0.05$) higher for the irradiated ham treatments (Table 1) compared to non-irradiated control regardless of length of storage period. This agrees with Houser and others (2003) who reported increased off-odor scores for irradiated (4.5kGy) cooked ham compared with control. However, that study, reported that off-odor decreased over time and was no longer significantly ($P>0.05$) different after 30 days of

storage. In addition, Zhu and others (2003) reported higher sulfur odor scores by a trained sensory panel for turkey ham irradiated at 2.0 kGy relative to controls. This sulfur odor was confirmed by analysis that showed increased production of sulfur-containing volatiles in the irradiated (2.0 kGy) turkey ham.

Table 1. The effect of irradiation treatment on off-odor scores for ham and frankfurters.

Irradiation dose (n=4)	Panel Scores	
	Ham	Frankfurters
0 kGy	60.4[a]	38.2
1.6 kGy	77.2[b]	45.0
S.E.M.	2.63	2.21

[a-b] Means within the same column with different superscripts are significantly different ($P<0.05$).
0 = no off-odor, 150 = intense off-odor

For the frankfurters, off-odor scores were not significantly different ($P>0.05$) for the main effect of irradiation treatment (Table 1) or storage period. These observations differ from reports by Terrell and others (1981a; 1981b; 1982) who showed a dose-dependent increase in off-odor production in irradiated (0, 8 and 32 kGy) pork/beef frankfurters. It appears that when lower doses of irradiation are used, off-odor production is not as easily detected in pork frankfurters. The significant ($P<0.05$) increase in off-odors for the ham as result of irradiation processing that was not observed for the frankfurters may be due to increased release of volatiles from the ham due to lower fat content. Jo and Ahn (1999) reported that fat content was negatively correlated with the release of volatiles from oil emulsions. On the other hand, this difference may be the result of greater smoke deposition during the smoking process or the addition of spices to the frankfurters. These additional ingredients in the frankfurters may have masked irradiation-induced off-odors.

Off-flavor scores were not significantly ($P>0.05$) different for ham due to irradiation treatment (Table 2) or length of storage period. This agrees with Zhu and others (2003) who reported that metallic, oxidation, sulfur and sweet flavors were not different ($P>0.05$) for turkey hams irradiated at 0, 1 and 2 kGy. However, irradiation treatment increased ($P<0.05$) off-flavor scores for the frankfurters (Table 2) and this effect did not change significantly ($P>0.05$) during storage. This agrees with Terrell and others (1981a; 1981b; 1982) who reported that irradiation significantly ($P<0.05$) increased off-flavor in pork/beef frankfurters in a dose-dependent manner (0, 8 and 32 kGy). It is possible that irradiation processing affected the non-meat portion of the frankfurters or the interaction between the meat and non-meat ingredients to result in a difference in flavor. The ham, which did not show a change in flavor scores, did not have spices added and was not smoked. On the other hand, differences in size and solubility of proteins due to processing methods may also contribute to flavor differences. During the manufacturing process, a larger percentage of the total salt-soluble proteins are extracted in frankfurters compared with ham. This extraction is necessary so that fat globules can be bound within the gel matrix of the frankfurter. The protein extracted in the frankfurters combined with changes to structure due to chopping would greatly increase the surface area of the salt soluble proteins compared with the ham. This change in structure may allow for increased oxidation and radiolysis of the proteins due to the increased surface area. It has recently been reported by Rowe and others (2004) that irradiation (6.4 kGy) increases protein oxidation in beef steaks. Additionally, it has been reported by Jo and Ahn (2000) that single amino acid side chains where more susceptible to radiolysis than intact proteins. It was suggested that the rigid structure of the intact protein offered some protection to the side chains on the amino acids within the protein. Furthermore, Jo and Ahn

(1999) reported that fat content was negatively correlated with volatile release from oil emulsions. Therefore, if volatile compounds where produced due to irradiation processing they may not be released to affect the odor profile of the frankfurters but are retained to affect the flavor profile of the frankfurters. Most likely, a combination of oxidation and radiolysis of the protein portion along with a decreased release of volatiles resulted in the off-flavor increase in the frankfurters.

Table 2. The effect of irradiation treatment on off-flavor scores for ham and frankfurters.

Irradiation dose (n=4)	Panel Scores	
	Ham	Frankfurters
0 kGy	48.7	43.2[a]
1.6 kGy	54.0	56.6[b]
S.E.M.	1.25	2.12

[a-b] Means within the same column with different superscripts are significantly different (P<0.05).
0 = no off-flavor, 150 = intense off-flavor

The volatile compounds, detected in the ham and frankfurter samples are listed in Table 3. Volatile compounds in the ham samples for which a significant (P<0.05) irradiation*time interaction was observed are listed in Table 4. A greater amount (P<0.05) of dimethyl disulfide was detected in the irradiated ham samples compared with non-irradiated control at week 0. Although the amount of dimethyl disulfide in the irradiated samples decreased (P<0.05) over time, it was still higher (P<0.05) than controls at week 8. This is consistent with Zhu and others (2003) who reported increased levels of dimethyl disulfide in turkey ham due to irradiation treatment. Furthermore, these authors, using a trained sensory panel, reported increased (P<0.05) sulfury odors for irradiated turkey ham compared with non-irradiated controls. It was concluded that sulfur-containing volatile formation as a result

of irradiation processing was one of the factors involved in off-odor development. Ahn (2002) reported that increased levels of sulfur-containing volatile compounds due to irradiation processing where the result of radiolytic degradation of methionine and cysteine. Additionally, the odor from the irradiated methionine and cysteine amino acid mixtures was characterized by a trained sensory panel as boiled cabbage, sulfury or rotten vegetable like. It was concluded that irradiation odor in meat products was the result of production of sulfur-containing volatiles as a result of radiolysis of sulfur-containing amino acids.

Volatile compounds that were significantly affected by irradiation treatment in the ham are listed in Table 5. Volatile compounds not detected in the control samples but which were present in the irradiated samples included 2-octene, toluene, heptane and trans-1-butyl-2-methylcyclopropanone. On the other hand, camphene was detected in the non-irradiated control but was not detected in the irradiated ham samples. Ethanol, 3-methyl butanal, 2-methyl butanal, 2-butanone and 2,3,4-trimethyl pentane increased ($P<0.05$) due to irradiation treatment. However, hexanal and heptanal decreased as a result of irradiation processing. Jo and Ahn (2000) and Ahn (2002) reported that irradiation processing of amino acids changed the volatile profiles of amino acid mixtures due to radiolysis. It was reported that while some volatile constituents of the amino acid mixtures increased due to irradiation, other volatile compounds decreased.

Table 3. Volatile compounds detected in ham and frankfurters.

Volatile compound	Ham	Frankfurter
2-Propanol	X	X
Ethanol	X	X
Hexanal	X	X
Heptanal	X	
Octanal	X	
Nonanal	X	X
Pentanal		X
3-Methyl butanal	X	X
2-Methyl butanal	X	X
2-Butanone	X	X
2-Propanone	X	X
Octane	X	X
Heptane	X	X
2-Octene	X	X
Pentane		X
Nonane		X
2,3,4-trimethyl pentane	X	X
3-Methyl-2-heptane	X	
Dimethyl disulfide	X	X
Carbon disulfide		X
Toluene	X	X
Trans-1-butyl-2-methylcyclopropane	X	
Camphene	X	X
Sabinene		X
Beta-pinene		X
Myrcene		X
Alpha-phellandrene		X
Delta-3-carene		X
Alpha-teroinene		X
1-Methyl-2-(1-methylethyl benzene)		X
Ocimene		X
Alpha-thujene		X
Alpha-pinene		X
Gamma-terpinene		X
Alpha-terpinolene		X
Camphor		X
p-Cymene	X	X
Limonine	X	X
Ehtyl acetate	X	
Acetonitrile	X	

Table 4. Interaction of irradiation treatment with storage time for production of volatiles in ham.

Volatile compound[1] (n=4)	Treatment	Week 0	Week 2	Week 4	Week 6	Week 8	S.E.M.
Dimethyl Disulfide	Control	1401[a]	1228[a]	1650[a]	2127[a]	804[a]	843
	Irradiated	10583[bz]	6182[by]	4688[by]	5473[by]	4521[by]	

[1]Total ion counts * 10^4

[a-b] Least squares means within the same column and volatile compound with different superscripts are significantly different (P<0.05).

[s-z] Least squares means within the same row with different superscripts are significantly different (P<0.05).

Table 5. Production of volatile compounds in ham as a result of irradiation processing.

Volatile compounds[1] (n=4)	Control	Irradiated	S.E.M.
Ethanol	1832[a]	7432[b]	848
3-Methyl butanal	1326[a]	1717[b]	63
2-Methyl butanal	854[a]	1627[b]	88
Heptanal	572[b]	418[a]	14
Hexanal	2029[b]	1530[a]	106
2-Butanone	1240[a]	1840[b]	57
Trans-1-butyl-2-Methylcyclopropanone	0[a]	402[b]	18
Heptane	0[a]	431[b]	11
2,3,4-trimethyl pentane	948[a]	1249[b]	56
Camphene	309[b]	0[a]	9
2-Octene	0[a]	318[b]	25
Toluene	0[a]	373[b]	32

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different (P<0.05).

A significant (P<0.05) interaction was present between irradiation and storage time for the presence of dimethyl disulfide and is listed in Table 6. Dimethyl disulfide was significantly (P<0.05) higher in the irradiated frankfurters at week 0 compared with non-irradiated controls. In addition, although dimethyl disulfide decreased (P<0.05) over time, it

was still significantly higher in irradiated frankfurters on week 8 compared with the non-irradiated controls on week 8.

Table 6. Interaction of irradiation treatment with storage time for production of volatiles in frankfurters.

Volatile compound[1] (n=4)	Treatment	Week 0	Week 2	Week 4	Week 6	Week 8	S.E.M.
Dimethyl disulfide	Control	245^{a}	335^{a}	271^{a}	298^{a}	284^{a}	115
	Irradiated	1294^{bxz}	1072^{bxz}	521^{awy}	790^{bwy}	715^{bwy}	

[1]Total ion counts * 10^4

[a-b] Least squares means within the same column with different superscripts are significantly different ($P<0.05$).

[w-z] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Volatile compounds that were significantly affected by irradiation processing for the frankfurters are listed in Table 7. All of the volatile compounds that were significantly different due to irradiation were significantly higher for the irradiated frankfurters compared with non-irradiated controls, with the exception of beta-pinene. Beta-pinene was significantly lower in the irradiated franks compared with non-irradiated control. In addition, 2-butanone was not present in the control frankfurters but was present in the irradiated frankfurters. Alcohols, aldehydes and ketones were all higher ($P<0.05$) in the irradiated frankfurters compared with non-irradiated controls. Since TBARS values were not increased due to irradiation processing for the frankfurters, the increase in alcohols, aldehydes and ketones was not entirely from lipid oxidation but were most likely a combination of lipid oxidation and the radiolysis of proteins and lipid. Jo and Ahn (2000) reported that irradiated oil emulsions had higher levels of hexanal compared to non-irradiated controls that increased in a dose dependent fashion indicating that some lipid oxidation had occurred. However,

Ahn (2002) reported that irradiation processing resulted in the radiolytic degradation of amino acids, which caused formation of aldehydes and ketones not present in the non-irradiated controls. Additionally, irradiation treatment caused increased levels of alcohols, aldehydes and ketones in the irradiated samples compared with non-irradiated controls for some of the amino acid treatments in the Ahn (2002) study.

Table 7. Production of volatile compounds in frankfurters as a result of irradiation processing.

Volatile compounds[1] (n=4)	Control	Irradiated	S.E.M.
2-Propanone	1956[a]	3883[b]	97
2-Butanone	0[a]	1162[b]	114
Hexanal	1594[a]	4544[b]	208
Pentanal	306[a]	1263[b]	52
Nonanal	728[a]	3058[b]	85
2-Methyl butanal	1172[a]	1344[b]	30
Octane	650[a]	1217[b]	69
2-Octane	157[a]	386[b]	26
Pentane	1431[a]	1846[b]	76
Nonane	311[a]	1713[b]	207
Camphene	11388[a]	25052[b]	1628
Toluene	188[a]	329[b]	24
Beta-pinene	20122[b]	9609[a]	581
Ocimene	3762[a]	6232[b]	387
Delta-3-carene	3806[a]	4411[b]	127
Alpha-terpinolene	3935[a]	5082[b]	134

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Conclusions

Irradiation processing did not affect color or TBARS values for ham or all-pork frankfurters. However, irradiation processing affected odor characteristics of the ham and the flavor properties of the frankfurters regardless of storage length. In addition, irradiation

processing increased the amount of volatiles present in both the ham and frankfurters. Although the concentration of volatiles increased in both products, some of the volatile compounds affected were much different in the ham compared with the frankfurters. Furthermore, a greater number of volatile compounds were affected in the frankfurters compared with the ham. Irradiation processing clearly altered the composition of volatile compounds of these products, which probably explains the changes in odor and flavor. However, more research is necessary to determine the source of the change in volatiles and how these changes might be controlled.

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CHAPTER 4. THE EFFECTS OF IRRADIATION ON COLOR, ODOR, FLAVOR AND PRODUCTION OF VOLATILES OF READY-TO-EAT BEEF, CHICKEN AND TURKEY

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Abstract

Ready-to-eat meat products were manufactured with beef, chicken or turkey, and were irradiated at 1.6 kGy. The products included; corned beef, roast beef, all-beef frankfurters, chicken roll, all-chicken frankfurters, turkey roll, cured turkey roll and all-turkey frankfurters. Each of the products was evaluated for color, odor, flavor and volatile compounds. Irradiation treatment did not significantly affect color scores for any of the products except the turkey roll. Turkey roll a* (redness) values were increased due to irradiation treatment. Off-odor scores increased due to irradiation processing for corned beef, roast beef, chicken roll, cured turkey roll, and turkey frankfurters. Off-odor scores were not significantly different due to irradiation treatment for the turkey roll, beef frankfurters or chicken frankfurters. Off-flavor scores were increased by the irradiation treatment for the cured turkey roll but no difference was observed for any of the other products tested. Irradiation processing increased the production of dimethyl disulfide for all of the products with the exception of the beef frankfurters. In addition, some of the volatiles present in the beef frankfurter spice blend were increased in the irradiated beef frankfurters. In general, while changes in color were not observed due to irradiation treatment, odor, flavor and production of volatiles were affected in most of the products. Therefore, irradiation processing to control microbial growth in ready-to-eat meat products should be

approached with caution because specific effects will depend on product type and species of raw meat materials that are used to manufacture the products.

Keywords: Ready-to-eat meat, color, odor, flavor, volatiles

Introduction

The United States Department of Agriculture (USDA) has a zero tolerance policy in place for the presence of *Listeria monocytogenes* in ready-to-eat meats (USDA 1989). This policy has resulted in recalls of products such as frankfurters and sliced luncheon meats (USDA 2004). Although this pathogen is eliminated from ready-to-eat (RTE) meat products using a proper thermal process (Carlier and others 1996), it can be reintroduced to the finished products during the slicing and packaging processes (Wang and Muriana 1994). The USDA recently established new regulations for the control of *L. monocytogenes* in RTE meat products (USDA 2003). These regulations for the control of *L. monocytogenes* propose the use of post-lethality treatments by meat processing establishments to eliminate the pathogen and ensure compliance. Studies have demonstrated the efficacy of ionizing irradiation for the elimination of pathogenic bacteria from pre-cooked meats (Fu and others 1995; Thayer and others 1998). However, the use of irradiation is not currently approved for RTE meats.

Although irradiation would be an effective post-lethality treatment for RTE meats changes in the characteristic sensory properties of these products have been reported (Houser and others 2003; Zhu and others 2003). Significant changes in meat flavor and aroma have been reported even at irradiation doses as low as 2.0 kGy (Shay and others 1988). Terrell and others (1981a; 1981b) reported increasing off-odor scores for frankfurters as irradiation dose increased from 0 to 8.0 kGy. Houser and others (2003) reported that a trained sensory

panel detected higher ($P<0.05$) off-odor scores on sliced RTE ham irradiated at 4.5 kGy when compared with non-irradiated ham at day 0. The off-odor was not significantly ($P>0.05$) different after 30 days of storage.

Changes in the characteristic flavor of RTE meats treated with irradiation have also been reported. A trained sensory panel detected differences in sulfur odor/flavor scores in RTE turkey ham treated with 2.0 kGy of irradiation (Zhu and others 2003). Gas chromatography was used to measure the amount of volatile compounds present in the turkey ham and confirm the differences in sulfur odor/flavor scores detected by the trained sensory panel. The results of the study showed a significant ($P<0.05$) increase in dimethyl disulfide and production of carbon disulfide in the irradiated samples. Ahn (2002) proposed that the off-odors produced in irradiated meats are the result of the radiolytic degradation of sulfur-containing amino acids.

RTE meats are manufactured with many different species of meat raw materials including beef, chicken and turkey, and are manufactured with a variety of spices and processing procedures. Further, RTE meats vary widely in proximate composition and may or may not be cured by the addition of sodium nitrite. There is also evidence that irradiation processing may not affect meat from different species in the same fashion. Nanke and others (1998; 1999) reported that changes in fresh meat color as a result of irradiation treatment were dependent upon species. In addition, Terrell and others (1982) found that the production of off-flavors in frankfurters as a result of irradiation processing was dependent upon the raw meat species used in the formulation of the frankfurters. Consequently it is reasonable to hypothesize that irradiation processing could affect the quality of RTE meats manufactured with different species differently. Therefore, the objectives of this research

were to determine the effect of irradiation processing on quality characteristics of some of the most common types of RTE meat products that are produced in the US, using beef, chicken or turkey as raw meat materials.

Materials and Methods

A total of eight different types of RTE meats were manufactured using beef, chicken or turkey species as meat raw materials. Products manufactured included roast beef, corned beef, beef frankfurters, chicken roll, chicken frankfurters, turkey roll, cured turkey roll, and turkey frankfurters. Current industry processing techniques and ingredients were used in the manufacture of each of the RTE products.

Corned beef was manufactured using *biceps femoris* muscles obtained from a local supplier. The beef muscles were trimmed free of external fat and subsequently injected (Townsend model P192-270, Townsend Eng., Des Moines, IA., U.S.A.) to 120% of initial weight with a curing solution consisting of 88.9% water, 6.04% salt, 2.2% dextrose, 1.7% phosphate blend (Brifisol 450 Super, BK Giulini Corp., Simi Valley, CA., U.S.A.), 0.75% spice oleoresins (A.C. Legg Packing Co., Birmingham, AL., U.S.A.), 0.27% sodium erythorbate and 0.1% sodium nitrite. After injection, samples were transferred to vacuum tumblers (DVTS Model 50, Daniels Food Equip. Inc., Parkers Prairie, MN., U.S.A.) and vacuum-tumbled for 20 minutes. Additional curing brine was added to the tumblers when necessary to attain the 120% added weight of brine. After tumbling was completed, the injected muscles were transferred to cook-in bags (Cryovac CN590, Cryovac Sealed Air Corp., Duncan, SC., U.S.A.) and vacuum packaged. The cook-in bags had an O_2 transmission rate of 20 cc/m^2/24 hr at 1 atm, 22.8°C and 0% relative humidity (RH). After

packaging, the samples were transferred to a thermal processing unit (ALKAR, Lodi, WI., U.S.A.) and thermally processed until an internal temperature of 73.8°C was achieved. After thermal processing, the corned beef was chilled at 2-4°C for 12-18 hours.

Roast beef was manufactured with fresh *semimembranosus* muscles obtained from a local supplier. External fat was trimmed from the beef muscles and then the muscles were injected (Townsend model P192-270, Townsend Eng., Des Moines, IA., U.S.A.) to 120% of initial weight with a seasoning solution. The seasoning solution consisted of 91.1% water, 4.13% salt, 1.91% dextrose, 1.77% phosphate blend (Brifisol 512, BK Giulini Corp., Simi Valley, CA., U.S.A.) and 1.09% spice oleoresins (A.C. Legg Packing Co., Birmingham, AL., U.S.A.). After injection, samples were transferred to vacuum tumblers (DVTS Model 50, Daniels Food Equip. Inc., Parkers Prairie, MN., U.S.A.) and vacuum-tumbled for 20 minutes. Additional seasoning brine was added to the tumblers when necessary to attain the 120% added weight. After tumbling was completed, the injected muscles were transferred to similar cook-in bags to those used for the corned beef and vacuum packaged. After packaging, the samples were transferred to a thermal processing unit (ALKAR, Lodi, WI., U.S.A.), thermally processed to an internal temperature of 54.4°C and held at that temperature for 45 minutes. After thermal processing, the roast beef was chilled at 2-4°C for 12-18 hours.

Beef frankfurters were manufactured with 90% lean trimmings and 50% lean trimmings, formulated to yield a finished 70% lean content. The beef frankfurter formulation consisted of the following ingredients; 73% beef trimmings, 21.2% ice/water, 2.0% salt, 1.46% corn syrup solids, 1.0% dextrose, 0.71% spices (A.C. Legg Packing Co., Birmingham, AL., U.S.A.), 0.35% phosphate blend, 0.183% curing salt (6.25% sodium nitrite) and 0.04%

sodium erythorbate. The beef frankfurters were manufactured using a vacuum bowl cutter (Krämer & Grebe Model VSM 65, Krämer & Grebe GmbH & Co. KG., Biendenkopf-Wallau, Germany) to form the meat batter. After chopping was completed, the meat batter was transferred to a rotary vane vacuum-filling machine with linking attachment (Risco SPA, Thiene, Italy), and stuffed into 26 mm inedible fibrous casings (Wienie-Pak, Teepak LLC., Lisle IL., U.S.A.). After stuffing, the raw beef frankfurters were held for 2-6 hours at 2-4°C to facilitate cured color development. The raw beef frankfurters were then transferred to a thermal processing unit (ALKAR, Lodi, WI., U.S.A.), smoked and thermally processed to an internal temperature of 71.1°C. After thermal processing, the franks were chilled for 12 hours at 2-4°C, then peeled (Townsend model 2600, Townsend Eng., Des Moines, IA., U.S.A.) before vacuum packaging.

The total meat block for the chicken and turkey frankfurters was formulated entirely with frozen mechanically separated poultry, obtained from regional poultry processors. The poultry frankfurter formulations consisted of 78.7% frozen mechanically separated poultry, 16.0% ice/water, 1.8% salt, 1.46% corn syrup solids, 1.0% dextrose, 0.71% spices (A.C. Legg Packing Co., Birmingham, AL., U.S.A.), 0.35% phosphate blend, 0.196% curing salt (6.25% sodium nitrite) and 0.043% sodium erythorbate. Prior to processing, the frozen mechanically separated meat blocks were tempered at 0-2°C for 12 hours. After tempering, the blocks of raw mechanically separated poultry products were flaked (Butcher Boy Model GMF, Lasar MFG Co., Los Angeles, CA., U.S.A.). The poultry frankfurters were manufactured in the same fashion as the beef frankfurters.

The poultry rolls (chicken roll, turkey roll and cured turkey roll) were manufactured with fresh/frozen boneless breast meat that was obtained from a local supplier. Ninety

percent of the meat was ground through a kidney plate and 10% was ground through a 3.1 mm plate (Biro MFG Co. Marblehead, OH, U.S.A.). The chicken roll formulation consisted of 70.7% coarse ground chicken breast, 7.07% finely ground chicken breast, 15.0% water, 2.0% dextrose, 3.0% potassium lactate solution (60% potassium lactate), 1.75% salt, 0.35% phosphate blend (Brifisol 960, BK Giulini Corp., Simi Valley, CA., U.S.A.) and 0.14% spices (A.C. Legg Packing Co., Birmingham, AL., U.S.A.). The turkey roll consisted of 70.7% coarse ground turkey breast, 7.07% finely ground turkey breast, 15.0% water, 2.0% dextrose, 3.0% potassium lactate solution (60% potassium lactate), 1.75% salt, 0.35% phosphate blend (Brifisol 960, BK Giulini Corp., Simi Valley, CA., U.S.A.) and 0.14% spices (A.C. Legg Packing Co., Birmingham, AL., U.S.A.). The cured turkey roll included 70.7% coarse ground turkey breast, 7.07% finely ground turkey breast, 15.0% water, 2.0% dextrose, 3.0% potassium lactate solution (60% potassium lactate), 1.60% salt, 0.35% phosphate blend (Brifisol 450 Super, BK Giulini Corp., Simi Valley, CA., U.S.A.), 0.15% curing salt (6.25% sodium nitrite), 0.14% spices (A.C. Legg Packing Co., Birmingham, AL., U.S.A.) and 0.043% sodium erythorbate. After grinding, the raw ground poultry breast meat was placed into a vacuum mixer (Higashimoto Model 20, Higashimoto Kikai Co. Ltd. Yamazoe, Nara, Japan), and vacuum-mixed for 20 minutes with all non-meat ingredients. After mixing was completed, the meat mixture was transferred to a rotary-vane vacuum-filling machine (Risco SPA, Thiene, Italy) and stuffed into 11.5 cm diameter impermeable fibrous casings (CMVP, Teepack LLC., Lisle, IL., U.S.A.). After stuffing, the poultry rolls were transferred to a thermal processing oven (Maurer AG, Reichenau, Germany) and cooked at 79.4°C with 100% RH for the entire process until the internal temperature of the

product reached 71.1°C. After thermal processing, the poultry rolls were chilled for 12 hrs at 2-4°C.

The corned beef, roast beef, chicken roll, turkey roll, and cured turkey roll products were each sliced (Bizerba Model SE12D Slicer, Bizerba GmbH & Co. KG., Balingen, Germany) to a 1.7 mm thickness, placed in barrier bags (Cryovac B540, Cryovac Sealed Air Corp., Duncan, SC., U.S.A.) and vacuum-packaged (Multivac Model A6800 vacuum packager, Multivac Inc., Kansas City, MO., U.S.A.). The packaging film had an O_2 transmission rate of 3-6 cc/m^2/24 hr at 1 atm, 4.4°C and 0% RH, and a water vapor transmission rate of 0.5-0.6 g/645 cm^2/24 hr and 100% RH. The resulting packages contained a total of 10 slices in each package for an overall thickness of 1.7 cm.

The beef, chicken, and turkey frankfurters were placed in barrier bags (Cryovac B540, Cryovac Sealed Air Corp., Duncan, SC., U.S.A.) after peeling, and vacuum packaged using the same packaging film described previously. The resulting packages contained a single layer of frankfurters consisting of 8 frankfurters per package.

After packaging all of the samples were randomly assigned to 0 or 1.6 kGy treatments and were sent under refrigerated conditions to SureBeam Corporation (Glendale Heights, IL., U.S.A.). Upon arrival at SureBeam Corp., the products were maintained at 2-4°C for 1-3 days until irradiation processing. Samples were irradiated by an electron beam accelerator (SureBeam Corp. Glendale Heights, IL., U.S.A.) to an average absorbed dose of 1.6 kGy with a maximum/minimum dose ratio of 1.21. After irradiation treatment, samples were returned under refrigerated conditions to the Iowa State Meat Laboratory and stored in cardboard boxes at 2-4°C until the products could be analyzed. The samples were analyzed for color, odor, flavor, and production of volatiles immediately after they were returned to

the Iowa State Meat Laboratory, which was between 2-5 days after irradiation processing was completed.

Color measurements were conducted using a Hunterlab Labscan colorimeter (Hunter Associated Laboratories Inc., Reston, VA., U.S.A.). The Hunterlab Labscan colorimeter was standardized using the same packaging material as used on the samples, placed over the white standard tile. Values for the white standard tile were X=81.72, Y=86.80 and Z=91.46. Illuminate A, 10° standard observer with a 2.54 cm viewing area and 3.05 cm port size was used to analyze the roast beef, corned beef, chicken roll, turkey roll, and cured turkey roll samples, and a 0.64 cm viewing area and 1.02 cm port size was used to analyze the internal color of frankfurter samples. Commission International d'Eclairage (CIE) L* (lightness), a* (redness), and b* (yellowness) measurements were taken at 4 randomly selected areas on the samples and the resulting average was used in data analysis (Hunt and others 1991). All of the products were measured while under vacuum-packaged conditions with the exception of the internal color of the frankfurters. Internal color of frankfurters was measured after slicing the frankfurters in half lengthwise and immediately measuring the internal color.

Proximate composition was determined on all products including crude fat (ether extract method, AOAC 1990a), moisture (air oven drying method, AOAC 1990b) and crude protein (combustion method, AOAC 1993). In addition, pH of the RTE products was determined by blending the samples with water in a 1:9 ratio, then measuring the pH with a pH/ion meter (Accumet 925: Fisher Scientific, Fair Lawn, NJ., U.S.A.) equipped with an electrode (Accumet Flat Surface Epoxy Body Ag/AgCl Combination Electrode Model 13-620-289, Fisher Scientific, Fair Lawn, NJ., U.S.A.) according to the method of Sebranek and others (2001).

Samples used for odor analysis were taken out of the package immediately after opening, cut into pieces, then placed into plastic dishes with covers. Samples used for flavor analysis were presented to the panelists separately from the samples used in the odor analysis. The sliced products were evaluated by the panelists without reheating, which would be characteristic of their intended use. The frankfurters were heated on an electric range top in boiling water and were subsequently served warm to the panelists, which would be characteristic for their intended use. Trained panelists (10-12), made up of Iowa State University students and staff, were used for each session. Panelists were trained to distinguish between samples irradiated at 0 and 8 kGy. For training, non-irradiated samples were used to represent no off-odor/off-flavor and 8 kGy samples were used to represent distinct off-odor/off-flavor. This permitted panelists to distinguish irradiation odors/flavors from normal odors/flavors. Panelists evaluated experimental samples for odor using a line scale with graduations from 0-150 mm, where 0 represented no off-odor and 150 represented intense off-odor. Additionally, panelists evaluated experimental samples for flavor using a line scale with graduations from 0-150 mm, where 0 represented no off-flavor and 150 represented intense off-flavor.

The production of volatiles was analyzed using a Solatek 72 Multimatrix-Vial Autosampler/Sample Concentrator 3100 (Tekmar-Dohrmann, Cincinnati, OH., U.S.A.) connected to a gas chromatograph/mass spectrometer (GC/MS; Model 6890/5973, Hewlett-Packard Co., Wilmington, DE., U.S.A.) according to the method of Ahn and others (2001). The RTE meat samples (3 g) were placed in a 40-mL sample vial, flushed with helium gas (40 psi) for 3 s and then capped airtight with a Teflon*fluorocarbon resin/silicone septum (I-Chem Co., New Castle, DE., U.S.A.). The maximum waiting time for a sample in a loading

tray (4°C) was less than 2 h to minimize oxidative changes before analysis. The meat sample was purged with helium (40 mL/min) for 14 min at 40°C. Volatiles were trapped using a Tenax/charcoal/silica column (Tekmar-Dohrmann, Cincinnati, OH., U.S.A.) and desorbed for 2 min at 225°C, focused in a cryofocusing module (-80°C) and then thermally desorbed into a column for 60 s at 225°C. A HP-624 column (7.5 m, 0.25 mm i.d., 1.4 μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.), a HP-1 column (60 m, 0.25 mm i.d., 0.25μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.) and a HP-Wax column (7.5 m, 0.25 mm i.d., 0.25 μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.) were connected using zero dead-volume column connectors (J &W Scientific, Folsom, CA, U.S.A.). A ramped oven temperature was used to improve volatile separation. The initial oven temperature of 0°C was held for 1.5 min. After that, the oven temperature was increased to 15°C at 2.5°C per min, increased to 45°C at 5°C per min, increased to 110°C at 20°C per min, then increased to 210°C at 10°C per min and held for 2.25 min at that temperature. Constant column pressure at 22.5 psi was maintained. The ionization potential of the MS was 70 eV and the scan range was 19.1 to 350 m/z. The identification of volatiles was achieved using the Wiley library (Hewlett-Packard Co., Wilmington, DE., U.S.A.). The area of each peak was integrated using ChemStation™ software (Hewlett-Packard Co., Wilmington, DE., U.S.A.) and the total peak area (total ion counts x 10^4) was reported as an indicator of volatiles generated from the samples. Volatiles of the spice blends that were used in the manufacture of the different RTE meat products were also measured by the same method.

A randomized complete block design consisting of 5-6 blocks (depending on product) and 2 irradiation doses (0, 1.6 kGy) was used. Statistical analysis was performed for all measurements using the Statistical Analysis System (1999-2001, Version 8.2, SAS Institute Inc., Cary, NC., U.S.A.) General Linear Model Procedure (Proc GLM). Least squares means were used to determine level of significance at $P<0.05$.

Results and Discussion

Mean proximate composition of the products were as follows: roast beef, 3.5% fat, 72.1% moisture and 22.4% protein; corned beef, 4.2% fat, 70.5% moisture and 22.2% protein; beef frankfurters, 31.1% fat, 51.8% moisture and 12.0% protein; chicken roll, 3.1% fat, 74.3% moisture, and 17.5% protein; chicken frankfurters, 12.8% fat, 68.4% moisture and 13.5% protein; turkey roll, 1.2% fat, 75.1% moisture and 19.2% protein; cured turkey roll, 1.1% fat, 75.1% moisture and 19.5% protein, and the turkey frankfurters 16.7% fat, 65.2% moisture and 12.2% protein. There were no significant ($P>0.05$) differences in pH due to irradiation treatment for any of the RTE meat products that were manufactured.

There were no significant ($P>0.05$) differences in CIE L*, a* and b* values for any of the RTE meat products as result of irradiation processing with the exception of the turkey roll. Turkey roll a* values were significantly ($P<0.05$) increased as result of irradiation processing. Least squares means for the irradiated turkey roll a* values were 10.7 and the non-irradiated control a* values were 9.2 (Standard Error of the Mean = 0.398). Nam and Ahn (2002) also reported increased redness values in irradiated (2.5 and 5.0 kGy) pre-cooked turkey breast meat. Further, Nam and Ahn (2002) also reported carbon monoxide production and increased reducing potential as result of irradiation processing. Therefore, these authors

concluded that carbon monoxide-heme pigment formation was one of the contributors to the irradiation-induced color change. In addition, Du and others (2003) reported a significant ($P<0.05$) increase in redness of cooked chicken breast when irradiated at 2.5 kGy compared with non-irradiated control. Our study did not show significant differences ($P>0.05$) in a* values for the chicken roll as result of irradiation treatment. This may be due to the lower irradiation dose that was used in the current study. These results for color were expected because most color changes in irradiated fresh meats have been shown to be dose-dependent and species-dependent (Nanke and others 1998; 1999). Therefore, it does not appear that irradiation processing at or below 1.6 kGy significantly impacted the color characteristics of the RTE meat products tested, with the exception of the turkey roll product.

Off-odor scores were significantly ($P<0.05$) increased for the irradiated corned beef, roast beef, chicken roll, cured turkey roll and turkey frankfurters compared with non-irradiated controls (Table 1). For example, on a scale of 0-150 with 0 representing no off/odor and 150 representing intense off/odor the least squares mean value of the irradiated corned beef was 47.0 compared with 33.5 for the non-irradiated corned beef. No significant differences ($P>0.05$) in off-odor production as result of irradiation processing were found for the turkey roll, beef frankfurters or chicken frankfurters. Houser and others (2003) reported increased off-odor scores for irradiated (4.5 kGy) cooked ham compared with non-irradiated controls. Because lower doses were used in the present study compared with Houser and others (2003), it seems likely that some products would not result in significant off-odor scores given that off-odor production in RTE meats has been reported to be dependent on irradiation dose level (Terrell and others 1981a; 1981b; 1982; Zhu and others 2003). All of the products tested in the present study included spices and it does not appear that the levels

of spice used in some of these products can completely mask the odors produced as a result of irradiation processing. In addition, it seems that the finely comminuted products such as the beef and chicken frankfurters were less susceptible to irradiation-induced off-odor production compared with the whole muscle products (corned beef and roast beef) and the chopped-and-formed products (poultry rolls). The difference in detectable odor for the frankfurters and other products tested could be due to differences in protein structure, the smoking process or the interaction between the meat portion and added spices. However, the differences in odor could also be due to the higher amount of fat and lower protein concentrations in the comminuted products compared with the whole muscle and chopped-and-formed products. Jo and Ahn (1999) reported that fat content was negatively correlated with the release of volatile compounds from oil emulsions. In addition, it has been reported by Ahn (2002) that irradiation odors are the result of radiolytic breakdown of amino acid side chains. It would therefore be reasonable to hypothesize that having a lower protein content combined with increased fat content would result in less volatile production and decreased release of volatiles which may have resulted in less off-odor production as viewed by the panelists in the high fat, low protein products such as the beef and chicken frankfurters. In light of these previously mentioned observations, it may be necessary to increase the fat content in turkey frankfurters to help control irradiation-induced off-odor production.

Off-flavor scores were not significantly different ($P>0.05$) due to irradiation processing with the exception of the cured turkey roll, which had significantly ($P<0.05$) higher off-flavor scores compared with non-irradiated controls (Table 2). The higher off-flavor scores for the cured turkey roll differ from the findings of Zhu and others (2003) who reported no difference ($P>0.05$) in metallic, oxidation, sulfur or sweet flavors in turkey ham

irradiated at 1 and 2 kGy compared with non-irradiated controls. In the current study, turkey breast was used to formulate the cured turkey roll compared with turkey thigh meat used in the Zhu and others (2003) study. The differences in muscle types used between the current study and the Zhu and others (2003) report may explain the difference in off-flavor results. This may be the case as Du and others (2003) reported lower ($P<0.05$) consumer preference scores for flavor acceptability when cooked chicken breast roll was irradiated at 2.5 kGy.

Table 1. The effect of irradiation treatment on odor scores of RTE meats.

Product	Control	Irradiated (1.6 kGy)	S.E.M.
Corned beef (n=6)	33.5[a]	47.0[b]	2.62
Roast beef (n=6)	46.4[a]	61.3[b]	3.20
Beef frankfurters (n=5)	42.5	39.5	2.41
Chicken roll (n=5)	32.6[a]	53.1[b]	3.44
Chicken frankfurters (n=5)	31.9	37.1	2.47
Turkey roll (n=5)	47.8	55.7	6.26
Cured turkey roll (n=5)	35.7[a]	48.6[b]	1.40
Turkey frankfurters (n=6)	35.1[a]	44.4[b]	0.901

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).
0 = no off-odor, 150 = intense off-odor

Table 2. The effect of irradiation treatment on flavor scores of RTE meats.

Product	Control	Irradiated (1.6 kGy)	S.E.M.
Corned beef (n=6)	29.8	40.0	5.80
Roast beef (n=6)	35.9	46.0	4.75
Beef frankfurters (n=5)	38.9	45.0	3.47
Chicken roll (n=5)	35.7	44.0	2.63
Chicken frankfurters (n=5)	28.9	29.1	3.25
Turkey roll (n=5)	34.0	48.5	5.76
Cured turkey roll (n=5)	28.7[a]	42.7[b]	0.856
Turkey frankfurters (n=6)	37.2	38.8	4.52

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).
0 = no off-flavor, 150 = intense off-flavor

Volatile compounds detected in RTE meats are listed in Table 3 and those detected in the spice blends used in the formulation of RTE meats are listed in Table 4. The production of volatiles as result of irradiation treatment for the corned beef is listed in Table 5. A significant increase ($P<0.05$) in volatile 3-methyl butanal and dimethyl disulfide resulted from irradiation processing. In addition, 2-butanone, 2-methyl butanal and toluene were detected in irradiated samples but were not detected in non-irradiated controls. Volatile compounds that were significantly ($P<0.05$) affected by irradiation processing in roast beef are listed in Table 6. Irradiation processing significantly increased 1-pentanol, hexanal, heptanal and nonanal. Furthermore, irradiation processing resulted in the formation of compounds not detected in non-irradiated roast beef including; 2-butanone, pentanal, 3-methyl butanal, 2-methyl butanal and dimethyl disulfide. However, 3-methylthio-1-propene and myrcene were lower ($P<0.05$) in the irradiated roast beef compared with control. Volatile compounds that were significantly ($P<0.05$) affected by irradiation processing in beef frankfurters are listed in Table 7. All of the aldehydes, ketones and alcohols that were significantly affected by irradiation processing were higher in the irradiated beef frankfurters than non-irradiated controls. In addition, dimethyl disulfide, methyl-2-propenyl disulfide and di-2-propenyl disulfide were lower in irradiated beef frankfurters compared with non-irradiated control. Furthermore, with the exception of 1-nonene, alkenes and alkanes were either undetected or lower ($P<0.05$) in non-irradiated controls than the irradiated beef frankfurters.

Table 3. Volatile compounds detected in RTE meats.

Volatile compound	Corned beef	Roast beef	Beef Frank	Chicken roll	Chicken frank	Turkey Roll	Cured Turkey roll	Turkey frank
1-Pentene		X	X					
Pentene			X	X	X	X		X
2-Propanone	X	X	X	X	X	X	X	X
Ethanol	X	X	X	X	X	X	X	X
2-Propanol			X	X	X	X	X	X
1-Pentanol		X	X	X	X	X	X	X
1-Butanol								X
2-Propen-1-ol		X			X			X
Terpinen-4-ol					X			
1-Octene-3-ol		X	X	X		X	X	X
2-Butanone	X	X	X	X	X	X		X
Hexanal	X	X	X	X	X	X	X	X
Heptanal	X	X	X	X	X	X	X	X
Propanal			X		X			X
Pentanal		X	X	X	X	X		X
Nonanal	X	X	X	X	X	X	X	X
3-Methyl butanal	X	X	X	X	X	X	X	X
2-Methyl butanal	X	X	X	X	X	X	X	X
Nonane			X					X
Heptane		X	X	X		X		X
2,3-Butadione	X	X	X					
Carbon disulfide			X		X			X
Dimethyl disulfide	X	X	X	X	X	X	X	X
Methyl-2-propenyl disulfide			X		X			X
Di-2-propenyl disulfide			X		X			X
Octane	X	X	X	X	X	X	X	X
1-Octane			X					
1-Decene			X					
1-Hexene			X					
1-Nonene			X					
2-Octene	X	X		X		X	X	
1-Methylthio propene		X						
3-Methylthio-1-propene	X	X	X		X			X
Toluene	X	X		X		X	X	X
Alpha-pinene		X	X	X	X	X		X
Beta-pinene		X	X	X	X	X		X
Myrcene		X	X	X	X	X	X	X
1-Phellandrene		X	X	X		X	X	X
3-Carene		X	X	X	X	X	X	X
Alpha-terpinene	X	X	X	X	X	X	X	X
Trans-beta-ocimene	X	X	X	X	X	X	X	X
Limonene	X	X	X	X	X	X	X	X
Para-cymene	X	X	X	X	X	X	X	X
Sabinene		X	X		X			X
Gamma-terpinene	X	X	X		X			X
Camphene		X	X		X			X
Linaool			X		X			X
Camphor			X		X			X
Alpha-thujene		X	X		X			X
Alpha-terpinolene		X	X		X			X
3,3'-Thiobis-1-propene			X		X			X
1,3,7-Octatriene			X		X			X

Table 4. Volatiles detected (X) in spices used in the manufacture of RTE meats.

Volatile compound	Corned beef	Roast beef	Beef frankfurter	Chicken, turkey and cured turkey rolls	Poultry frankfurter
3-Methyl pentane				X	
Ethanol	X	X	X	X	X
Hexane	X	X	X	X	X
3-Methyl butanal				X	
2-Methyl butanal				X	
Toluene	X			X	
Hexanal	X	X		X	
Trans-caryophyllene			X	X	
Heptanal	X			X	X
Alpha-thujene			X	X	X
Alpha-pinene		X	X	X	X
Beta-selinene			X	X	
Alpha-fenchene			X	X	X
Camphene				X	
Terpinolene				X	
Sabinene		X	X	X	X
Beta-pinene		X	X	X	X
Myrcene	X	X	X	X	X
1-Phellandrene		X	X	X	X
3-Carene		X	X	X	X
Alpha-terpinene	X	X	X	X	X
Limonene	X	X	X	X	X
Trans-beta-ocimene			X	X	X
Gamma-terpinene	X	X	X	X	X
Alpha-terpinolene		X	X	X	X
Nonanal	X	X	X		X
Benzaldehyde		X	X	X	X
Benzene				X	
Alpha-thujone				X	
Beta-ocimene	X		X		X
Pentyl benzene				X	
Linalool	X	X	X	X	X
Camphor			X	X	X
1-Phenyl ethanone	X	X	X	X	X
Terpineol-4		X	X	X	X

Table 5. Volatile compounds in irradiated corned beef.

Volatile compound[1] (n=6)	Control	Irradiated	S.E.M.
2-Butanone	0^{a}	1987^{b}	232
3-Methyl butanal	353^{a}	685^{b}	26
2-Methyl butanal	0^{a}	264^{b}	24
Dimethyl disulfide	255^{a}	1430^{b}	170
Toluene	0^{a}	291^{b}	58

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Table 6. Volatile compounds in irradiated roast beef.

Volatile compound[1] (n=6)	Control	Irradiated	S.E.M.
1-Pentanol	199^{a}	366^{b}	43
2-Butanone	0^{a}	2458^{b}	201
Hexanal	1647^{a}	4679^{b}	710
Heptanal	331^{a}	661^{b}	43
Pentanal	0^{a}	749^{b}	104
Nonanal	736^{a}	1361^{b}	136
3-Methyl butanal	0^{a}	479^{b}	10
2-Methyl butanal	0^{a}	283^{b}	6
Dimethyl disulfide	0^{a}	1387^{b}	192
3-Methylthio-1-propene	1187^{b}	541^{a}	103
Myrcene	974^{b}	488^{a}	128

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Volatile compounds that were significantly ($P<0.05$) affected by irradiation processing in the chicken roll are listed in Table 8. Pentane, 3-methyl butanal, dimethyl disulfide, toluene, 3-carene and trans-beta-ocimene were all higher for the irradiated chicken roll compared with non-irradiated controls. Para-cymene on the other hand, was lower in the irradiated product.

Table 7. Volatile compounds in irradiated beef frankfurters.

Volatile compound[1] (n=5)	Control	Irradiated	S.E.M.
1-Pentane	0[a]	736[b]	59
Pentane	409[a]	1212[b]	23
2-Propanone	2942[a]	4066[b]	195
Ethanol	2716[a]	4284[b]	15
2-Butanone	1068[a]	1954[b]	216
Hexanal	2138[a]	3146[b]	189
Heptanal	250[a]	618[b]	37
Pentanal	423[a]	791[b]	25
Nonanal	364[a]	593[b]	42
3-Methyl butanal	1190[a]	1474[b]	20
2-Methyl butanal	444[a]	630[b]	9
Nonane	0[a]	250[b]	11
Heptane	0[a]	527[b]	37
2,3-Butadione	0[a]	553[b]	104
Dimethyl disulfide	1729[b]	684[a]	206
Methyl-2-propenyl disulfide	1883[b]	724[a]	95
Di-2-propenyl disulfide	8777[b]	2010[a]	684
Octane	208[a]	793[b]	79
1-Octene	0[a]	310[b]	17
1-Decene	0[a]	257[b]	16
1-Hexene	0[a]	429[b]	15
1-Nonene	2275[b]	255[a]	325
Beta-pinene	3457[a]	3953[b]	85
Myrcene	830[a]	942[b]	23
3-Carene	2138[a]	2340[b]	36
Alpha-terpinene	1753[a]	2082[b]	52
Trans-beta-ocimene	573[a]	692[b]	23
Limonene	3831[a]	4230[b]	69
1-Phellandrene	624[a]	723[b]	13
Alpha-thujene	808[a]	1029[b]	26
Alpha-terpinolene	937[a]	1066[b]	13
3,3'-Thiobis-1-propene	0[a]	1478[b]	61

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Results for volatile compounds significantly ($P<0.05$) affected by irradiation processing in the chicken frankfurters are listed in Table 9. 2-butanone, propanal, dimethyl

disulfide, methyl-2-propenyl disulfide and di-2-propenyl disulfide increased for the irradiated chicken frankfurters compared with non-irradiated frankfurters. Additionally, myrcene and camphene were reduced in irradiated chicken frankfurters compared with non-irradiated control.

Table 8. Volatile compounds in irradiated chicken roll.

Volatile compound[1] (n=5)	Control	Irradiated	S.E.M.
Pentane	0[a]	2144[b]	212
3-Methyl butanal	428[a]	944[b]	101
Dimethyl disulfide	906[a]	6652[b]	491
Toluene	0[a]	322[b]	22
3-Carene	507[a]	2209[b]	208
Trans-beta-ocimene	191[a]	1058[b]	106
Para-cymene	4386[b]	806[a]	644

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Table 9. Volatile compounds in irradiated chicken frankfurters.

Volatile compound[1] (n=5)	Control	Irradiated	S.E.M.
2-Butanone	0[a]	1558[b]	131
Propanal	0[a]	1353[b]	182
Dimethyl disulfide	0[a]	2268[b]	284
Methyl-2-propenyl disulfide	235[a]	709[b]	75
Di-2-propenyl disulfide	921[a]	1842[b]	200
Myrcene	1217[b]	1026[a]	43
Camphene	296[b]	192[a]	22

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Table 10 displays the results for volatile compounds that were significantly ($P<0.05$) affected by irradiation processing of the turkey roll. Pentane, 3-methyl butanal, dimethyl

disulfide, toluene, 3-carene and trans-beta-ocimene were increased in the irradiated turkey roll compared with non-irradiated control. Again as noted for the chicken roll, para-cymene was lower in the irradiated samples. Results for the cured turkey roll are listed in Table 11. In this case heptanal, nonanal, dimethyl disulfide, toluene and trans-beta-ocimene were increased for the irradiated cured turkey roll, compared with non-irradiated control. Table 12 shows the volatiles for turkey frankfurters, where 2-butanone, 2-methyl butanal, nonane, heptane and dimethyl disulfide were all increased in the irradiated turkey frankfurters compared with non-irradiated control.

Dimethyl disulfide was a volatile compound that increased in all products with the exception of the beef frankfurters as a result of irradiation. This agrees with Du and others (2003) and Zhu and others (2003) who reported increased sulfur compounds including dimethyl disulfide in cooked poultry products as a result of irradiation processing. In addition, Zhu and others (2003) reported increased sulfur odors by a trained sensory panel. Zhu and others (2003) concluded that increased sulfur-containing volatiles present as result of irradiation treatment were the cause of changes in sulfur odor due to irradiation processing. This may also be the case in the present study, as most of the products had increased off-odors as result of irradiation treatment as well as increased production of sulfur-containing volatiles. Furthermore, irradiation treatment of beef frankfurters resulted in lower dimethyl disulfide, methyl-2-propenyl disulfide and di-2-propenyl disulfide compared with control and irradiation processing did not increase off-odor in the beef frankfurters. It seems likely that sulfur-containing compounds are one of the major compound groups responsible for changes in odor as a result of irradiation processing of RTE meats. The production of sulfur-containing volatiles as a result of radiolytic degradation of amino acid

side chains by irradiation processing has been reported by Ahn (2002). It was further reported by Ahn (2002) that methionine and cysteine were the amino acids that produced the sulfur-containing volatiles as a result of irradiation (5 kGy) and that these compounds produced irradiation odors described by a trained sensory panel as boiled cabbage, sulfury and rotten vegetable-like.

Table 10. Volatile compounds in irradiated turkey roll.

Volatile compound[1] (n=5)	Control	Irradiated	S.E.M.
Pentane	0^{a}	2144^{b}	213
3-Methyl butanal	428^{a}	944^{b}	101
Dimethyl disulfide	906^{a}	6652^{b}	491
Toluene	0^{a}	322^{b}	22
3-Carene	507^{a}	2209^{b}	208
Trans-beta-ocimene	191^{a}	1058^{b}	106
Para-cymene	4386^{b}	806^{a}	644

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Table 11. Volatile compounds in irradiated cured turkey roll.

Volatile compound[1] (n=5)	Control	Irradiated	S.E.M.
Heptanal	0^{a}	176^{b}	9
Nonanal	256^{a}	500^{b}	44
Dimethyl disulfide	677^{a}	3818^{b}	478
Toluene	0^{a}	254^{b}	23
Trans-beta-ocimene	133^{a}	403^{b}	49

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Volatiles found in the spice blends also seem to have been affected by irradiation treatment. For example, beta-pinene, myrcene, 3-carene, alpha-terpinene, trans-beta-

ocimene, limonene, 1-phellandrene, alpha-thujene and alpha-terpinolene which were present in the beef frankfurter spice blend (Table 4) increased ($P<0.05$) as a result of irradiation treatment in the beef frankfurters (Table 7).

Table 12. Volatile compounds in irradiated turkey frankfurters.

Volatile compound[1] (n=6)	Control	Irradiated	S.E.M.
Ethanol	2216[a]	3396[b]	56
2-Butanone	0[a]	553[b]	92
2-Methyl butanal	0[a]	482[b]	74
Nonane	0[a]	240[b]	25
Heptane	0[a]	378[b]	95
Dimethyl disulfide	683[a]	2202[b]	345

[1]Total ion counts * 10^4

[a-b] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

This observation may indicate that meat processing and/or irradiation processing caused changes in the structure of the spices used in the beef frankfurters, which increased their volatility. If processing increased the volatility of the spices in the beef frankfurters, it may be possible that off-odors and off-flavors were masked and hence undetectable by the panelists. More likely, a combination of decreased sulfur compounds and increased spice volatility resulted in no detectable off-odor or off-flavor in the irradiated beef frankfurters. However, it is unclear why sulfur compounds decreased in the irradiated beef frankfurters but increased in the corned beef and roast beef.

Conclusions

Irradiation processing did not affect color of RTE meat products with the exception of increased a* values in the turkey roll. However, irradiation treatment affected the odor

characteristics of corned beef, roast beef, chicken roll, cured turkey roll and turkey frankfurters. Additionally, irradiation changed the flavor characteristics of the cured turkey roll. The production of several volatiles was increased as a result of irradiation treatment for most compounds including dimethyl disulfide in particular. The beef frankfurters were the only product tested which showed decreased levels of dimethyl disulfide following irradiation. Moreover, volatiles from spices used in the formulation of the beef frankfurters were increased as a result of irradiation processing. Consequently, the effects of irradiation on RTE meat products are complex and each product type, spice blend and irradiation dose combination will most likely require independent evaluation for potential quality changes.

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CHAPTER 5. THE EFFECTS OF pH AND IRRADIATION PROCESSING ON THE PRODUCTION OF VOLATILE COMPOUNDS AND SENSORY PROPERTIES OF HAM

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Abstract

Hams were manufactured to achieve three different pHs in the finished products. Then, the hams were treated with irradiation at 0.0 kGy, 1.21 kGy, 2.34 kGy and 4.57 kGy average doses. The samples were evaluated for yields, purge lost, color and volatile composition. The aroma, off-aroma, flavor and off-flavors were evaluated by a trained sensory panel. A consumer panel evaluated the aroma and flavor of the ham. The color values were not affected by the pH or irradiation treatments. The pH treatments affected the yields and purge lost for the hams. Hexanal content increased with the high pH treatment while carbon disulfide decreased as the pH increased from 5.82 to 6.72. A significant increase in the production of dimethyl disulfide was observed when the ham was treated with irradiation doses of 2.34 kGy or higher. A significant interaction was observed between pH and irradiation treatment for flavor scores from the trained panel. The trained panelists did not find significant differences in flavor between the high pH and the low pH treatments when both samples were treated with irradiation. The consumer panel reported aroma and flavor scores significantly lower for the irradiated samples compared to the non-irradiated counterparts.

Keywords: Irradiation, pH, color, volatiles, aroma, flavor

Introduction

Pathogens such as *Listeria monocytogenes* can be eliminated from ready-to-eat (RTE) meat products using a proper thermal process (Carlier and others 1996). However, this pathogen can be reintroduced to the finished products during the slicing and packaging processes (Wang and Muriana 1994). Low storage temperature does not prevent the growth of pathogens such as *L. monocytogenes* once recontamination occurs (Beumer and others 1996). The United States Department of Agriculture (USDA) has a zero tolerance policy in place for the presence of *L. monocytogenes* in ready-to-eat (RTE) meats (USDA 1989). Several recalls of products such as frankfurters and sliced luncheon meats have been put in place due to the presence of *L. monocytogenes* in RTE meat products (USDA 2004). The USDA recently established new regulations for the control of *L. monocytogenes* in RTE meat products which propose the use of post-lethality treatments to eliminate the pathogen and ensure food safety (USDA 2003). Studies have demonstrated the efficacy of ionizing irradiation for the elimination of pathogenic bacteria from pre-cooked meats (Fu and others 1995; Thayer and others 1998). However, the use of irradiation is not currently approved for RTE meats.

Irradiation treatments (1.5-10 kGy) can be used to reduce and/or eliminate pathogenic, as well as, non-pathogenic bacteria that may be present in meat products (Thayer and others 1996; Olson 1995). However, changes in the characteristic sensory properties of these products have been reported (Houser and others 2003; Zhu and others 2004). Significant changes in meat flavor and aroma have been reported even at irradiation doses as low as 2.0 kGy (Shay and others 1988). Terrell and others (1981a; 1981b) reported increasing off-odor scores for frankfurters as irradiation dose increased from 0 to 8.0 kGy.

Houser and others (2003) reported that a trained sensory panel detected higher ($P<0.05$) off-odor scores on sliced RTE ham irradiated at 4.5 kGy when compared with non-irradiated ham at day 0. A trained sensory panel detected differences in sulfur odor/flavor scores in RTE turkey ham treated with 2.0 kGy of irradiation (Zhu and others 2004). Gas chromatography was used to measure the amount of volatile compounds present in the turkey ham and confirm the differences in sulfur odor/flavor scores detected by the trained sensory panel. The results of the study showed a significant ($P<0.05$) increase in dimethyl disulfide and production of carbon disulfide in the irradiated samples.

Dimethyl trisulfide was reported to be the main sulfur containing compound present in raw chicken meat treated with a medium dose (2.5 kGy) of ionizing irradiation (Patterson and Stevenson 1995). A higher concentration of aldehydes such as propanal, pentanal, hexanal have been reported in irradiated (2.5 kGy) and then cooked turkey meat stored for 7 days at 4°C (Ahn and others 1998). Also, an increase in the amount of carbonyl compounds was observed in pre-cooked, irradiated (18.6-27.9 kGy), canned pork chops and veal shoulder clods stored at 2°C. The same study revealed that the cooking process increased the concentration of carbonyls and hydrogen sulfides, followed by a further increase as a result of the irradiation treatment (Pearson and others 1959).

Factors such as pH, temperature, buffer capacity and the concentration of reactants influence the formation of 2-methyl-3-furanthiol and other compounds in model systems (Mottram and Madruga 1994). In model systems the production of pyrazines was favored by pHs above 5.5, while lower pHs favored the production of 2-methyl-3-furanthiol. These authors confirmed the importance of pH in the formation of volatile compounds in food with strong buffering capacity such as meat. Reducing the pH of meat below 5.0 promoted the

formation of thiols, mercaptoketones and some di- and trisulfides containing the 2-methyl-3-furanone group (Mottram and Madruga 1994).

Therefore, the purpose of this study was to study the changes in the concentration of volatiles, flavor and aroma of irradiated ham at different pHs.

Materials and Methods

Fresh porcine *biceps femoris* (ham) muscles were obtained from a meat processing plant in Iowa. The ham muscles were received free of external fat and packaged under vacuum. The experiment consisted of the following treatment combinations:

- Low pH, 0.0 kGy
- Low pH, 1.21 kGy
- Low pH, 2.34 kGy
- Low pH, 4.57 kGy
- Control pH, 0.0 kGy
- Control pH, 1.21 kGy
- Control pH, 2.34 kGy
- Control pH, 4.57 kGy
- High pH, 0.0 kGy
- High pH, 1.21 kGy
- High pH, 2.34 kGy
- High pH, 4.57 kGy

The muscles were ground (Biro MFG Co. Marblehead, OH., U.S.A.) using a 2.54 cm plate at the Iowa State University Meat Laboratory. The resulting ham pieces were then mixed together and randomly assigned by weight to the experimental units. This process was repeated 5 times resulting in 5 replications of the experiment. The separate meat blocks were then transferred to vacuum tumblers (DVTS Model 50, Daniels Food Equip. Inc., Parkers Prairie, MN., U.S.A.) and curing brine was added. Concentrations of curing ingredients in the ham products based on total meat block weight were 15.0% water, 2.5% sodium chloride, 1.5% sugar, 0.35% sodium phosphate (CuraFos Formula 11-2, Rhodia Inc., Cranbury, NJ., U.S.A.). The pH treatments applied to the hams were 0.15% sodium hydroxide (Sodium hydroxide pellets FCC CAS 1310-73-2 Voigt Global Distribution LLC, Kansas City, MO. U.S.A.), 0.35% encapsulated citric acid (CAP-SHURE® C-140 D-72 Balchem Corporation, Slate Hill, NY., U.S.A.) or 0.0% sodium hydroxide/encapsulated citric acid. The hams were tumbled under vacuum for 2 hours. After tumbling the hams were stuffed into 6.3 cm diameter impermeable fibrous casings (CMVP, Teepack LLC., Lisle, IL., U.S.A.) using a rotary-vane vacuum-filling machine (Risco SPA, Thiene, Italy).

The hams were transferred to a single truck thermal processing oven (Maurer AG, Reichenau, Germany) and held for 2 hours under refrigeration prior to cooking to facilitate cure color development. The hams were cooked with 100 % RH at 79.4°C to an internal temperature of 70°C. After thermal processing, the hams were chilled for 12 h at 2-4°C. Cooked yield % was calculated as cooked product weight loss divided by the raw weight, multiplied by 100.

The pH of the finished ham was determined by blending the samples with water in a 1:9 ratio, then measuring the pH with a pH/ion meter (Accumet 925: Fisher Scientific, Fair

Lawn, NJ., U.S.A.) equipped with an electrode (Accumet Flat Surface Epoxy Body Ag/AgCl Combination Electrode Model 13-620-289, Fisher Scientific, Fair Lawn, NJ., U.S.A.) according to the method of Sebranek and others (2001).

The hams were removed from the casings, sliced (Bizerba Model SE12D Slicer, Bizerba GmbH & Co. KG., Balingen, Germany) to a 1.7 mm thickness and packaged 7 slices per package for an overall package thickness of 1.2 cm. Slices of ham samples were vacuum-packaged using barrier bags (Cryovac B540, Cryovac Sealed Air Corp., Duncan, SC., U.S.A.; Multivac Model A6800 vacuum packager, Multivac Inc., Kansas City, MO., U.S.A.). The packaging film had an O_2 transmission rate of 3-6 cc/m^2/24 hr at 1 atm, 4.4°C, and 0% RH, and a water vapor transmission rate of 0.5-0.6 g/645 cm^2/24 hr and 100% RH. The hams were stored at 2-4°C until irradiation processing.

Irradiation of the ham samples was accomplished at the Iowa State University Meat Laboratory Linear Accelerator Facility. Samples were irradiated by an electron beam irradiator (Model CIRCE IIIR, Thomson CSF Linac., Saint Aubin, France) with an energy level of 10 MeV and a power level of 5.6 kW. The average dose rate for all the treatments was 56.9 kGy/min and the estimated overall average doses were 1.21 kGy, 2.34 kGy and 4.57 kGy with maximum/minimum doses of 1.36/1.07kGy, 2.62/2.06 kGy and 5.10/4.03 kGy respectively. Average absorbed doses were confirmed using 99% pure alanine dosimeters (Bruker-Biospin Corp., Billerica, MA., U.S.A.) measured by an electron paramagnetic resonance instrument (Model EMS 104, Bruker-Biospin, Karlsruhe, Germany). Following irradiation, samples were stored in cardboard boxes at 2-4°C until the products could be analyzed.

Purge loss (%) was calculated as product weight loss divided by the initial weight, multiplied by 100.

Color measurements were conducted immediately after irradiation processing (day 0) using a Hunterlab Labscan colorimeter (Hunter Associated Laboratories Inc., Reston, VA., U.S.A.). The Hunterlab Labscan colorimeter was standardized using the same packaging material as used on the samples, placed over the white standard tile. Values for the white standard tile were X=81.72, Y=86.80 and Z=91.46. Illuminate A, 10° standard observer with a 2.54 cm viewing area and a 3.05 cm port size were used to analyze the ham samples. Commission International d'Eclairage (CIE) L* (lightness), a* (redness) and b* (yellowness) measurements were taken at 2 randomly selected areas on each of the samples measured and the resulting average was used in data analysis.

The production of volatiles was analyzed using a Solatek 72 Multimatrix-Vial Autosampler/Sample Concentrator 3100 (Tekmar-Dohrmann, Cincinnati, OH., U.S.A.) connected to a gas chromatograph/mass spectrometer (GC/MS; Model 6890/5973, Hewlett-Packard Co., Wilmington, DE., U.S.A.) according to the method of Ahn and others (2001). The RTE meat samples (3 g) were placed in a 40-mL sample vial, flushed with helium gas (40 psi) for 3 s and then capped airtight with a Teflon*fluorocarbon resin/silicone septum (I-Chem Co., New Castle, DE., U.S.A.). The maximum waiting time for a sample in a loading tray (4°C) was less than 2 h to minimize oxidative changes before analysis. The meat sample was purged with helium (40 mL/min) for 14 min at 40°C. Volatiles were trapped using a Tenax/charcoal/silica column (Tekmar-Dohrmann, Cincinnati, OH., U.S.A.) and desorbed for 2 min at 225°C, focused in a cryofocusing module (-80°C) and then thermally desorbed into a column for 60 s at 225°C. A HP-624 column (7.5 m, 0.25 mm i.d., 1.4 μm nominal,

Hewlett-Packard Co., Wilmington, DE., U.S.A.), a HP-1 column (60 m, 0.25 mm i.d., 0.25μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.) and a HP-Wax column (7.5 m, 0.25 mm i.d., 0.25 μm nominal, Hewlett-Packard Co., Wilmington, DE., U.S.A.) were connected using zero dead-volume column connectors (J &W Scientific, Folsom, CA, U.S.A.). A ramped oven temperature was used to improve volatile separation. The initial oven temperature of 0°C was held for 1.5 min. After that, the oven temperature was increased to 15°C at 2.5°C per min, increased to 45°C at 5°C per min, increased to 110°C at 20°C per min, then increased to 210°C at 10°C per min and held for 2.25 min at that temperature. Constant column pressure at 22.5 psi was maintained. The ionization potential of the MS was 70 eV and the scan range was 19.1 to 350 m/z. The identification of volatiles was achieved using the Wiley library (Hewlett-Packard Co., Wilmington, DE., U.S.A.). The area of each peak was integrated using ChemStation^{TM} software (Hewlett-Packard Co., Wilmington, DE., U.S.A.) and the total peak area (total ion counts x 10^4) was reported as an indicator of volatiles generated from the samples.

A trained sensory panel was used to evaluate quality attributes of the following treatments:

- Low pH, 0.0 kGy
- Low pH, 2.21 kGy
- Control pH, 0.0 kGy
- Control pH, 2.21 kGy
- High pH, 0.0 kGy
- High pH, 2.21 kGy

Ten panelists were recruited from the faulty, staff, and students of Iowa State University. Panelists were trained to evaluate ham aroma, off-aroma (irradiated), ham flavor, off-flavor (irradiated), sourness, and saltiness/salty aftertaste. Samples selected to exhibit the above sensory attributes were used to familiarize the panelists with the attributes to be evaluated, the testing techniques to be used during the evaluation process, and the computer software scoring system.

Panelists were served individually packaged ham slices at 4°C on trays that had been pre-cooled. The bags were labeled with random three-digit codes. The samples were served simultaneously and sampling order was randomized. Panelists were instructed to cut open a bag approximately one inch above the sample, smell the sample, and evaluate its aroma. Panelists then cut the sample into quarters and evaluated the flavor attributes.

Five sessions, each session representing one of five replications, were conducted. Panelists evaluated six samples each session. Water and unsalted crackers were available to panelists. Panelists were instructed to rinse their mouth with water between samples. Testing was conducted in partitioned booths and under red fluorescent lighting conditions. For each attribute, a line scale (numerical value of 15 units), labeled with descriptors representing low intensity at the left (none) and high intensity at the right (intense), was used for scoring. Data was collected by using a computerized sensory data collection system (Compusense five, v 4.4, Compusense, Inc. Guelph, Ontario, Canada N1H3N4).

A consumer test of the ham was conducted on the following treatments:

- Control pH, 0.0 kGy
- Low pH, 0.0 kGy
- Low pH, 2.21 kGy

One hundred participants, 18 years of age or older, were asked to evaluate the aroma and flavor of the three ham samples. Participants received individually packaged ham slices at 4°C on trays that had been pre-cooled. The ham slices represented samples from five replications. The bags were labeled with random three-digit codes. The samples were served simultaneously and sampling order was randomized. Participants cut open a bag approximately one inch above the sample, smelled the sample, and evaluated its aroma. Participants were then instructed to cut the sample into bite-size pieces and to evaluate the flavor. For each attribute, a line scale (numerical value of 15 units), labeled with descriptors representing low intensity at the left (none) and high intensity at the right (intense), was used for scoring. Participants completed the test by using a computerized scoring system (Compusense five, v 4.4, Compusense, Inc. Guelph, Ontario, Canada n1H3N4).

Participants were instructed to rinse their mouths with water before starting to taste and between samples. Samples were evaluated in partitioned booths under fluorescent lighting conditions. Each participant evaluated all three samples.

The experiment design was a randomized complete block design consisting of 3 pHs and 4 irradiation treatments was used. Statistical analysis was performed for all measurements using the Statistical Analysis System (1999-2001, Version 8.2, SAS Institute Inc., Cary, NC., U.S.A.) Mixed Model procedure (Proc Mixed). The main effects were pH, irradiation treatment and replication. The random effect were replication*pH, replication*irradiation treatment and replication*pH*irradiation treatment. Least squares means were used to determine level of significance at $P<0.05$ after adjustment for all pair-wise comparisons using the Tukey-Kramer procedure.

Results and discussion

The average pH of the hams was 5.82 (low), 6.36 (control) and 7.20 (high). The cooking yields of the low pH ham was significantly ($P<0.05$) lower than the control and the high pH ham. The purge content was significantly ($P<0.05$) lower for the high pH treatment relative to the other pH treatments. No difference in purge lost was observed between the control and low pH treatments.

Table1. Effect of pH on yield and purge of ham

Measurement (n = 5)	pH 5.82	pH 6.36	pH 6.72	S.E.M.
% Yield	96.8^{a}	97.2^{ab}	98.2^{b}	0.35
% Purge	4.98^{b}	4.76^{b}	4.11^{a}	0.12

$^{a-b}$ Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

There were no significant ($P<0.05$) differences in CIE L*, a* and b* values due to the pH or irradiation treatments. Fu and others (1995) found similar results when ham was treated with an irradiation dose of 1.8 kGy. However, Houser and others (2003, 2005) reported significantly lower CIE L* values and an interaction between day and irradiation for CIE a*/b* ratios of hams irradiated with a dose of 4.5 kGy when compared to control.

The volatile compounds detected in the hams are listed in Table 2. Table 2 also indicates whether the volatiles were affected by the pH treatments, irradiation processing or both. Hexanal, 2-propanone and carbon disulfide were affected by the pH treatments. Irradiation processing affected the production of ethanol, heptanal, octane, 1-hexene, 1-heptene, 1-octene, 1-pentane, hexane, 2,3,5-trimethyl hexane, 2,2,7-trimethyl decane,

dimethyl disulfide and toluene. 3-Methyl butanal, 2-methyl butanal, 2-methyl propanal, 2-butanone and heptane were affected by both treatments.

Table 2. Volatile compounds detected in ham.

Volatile compound	pH[a]	Irradiation[b]
2-Propanol		
Ethanol		X
Hexanal	X	
Heptanal		X
Pentanal		
3-Methyl butanal	X	X
2-Methyl butanal	X	X
2-Methyl propanal	X	X
2-Butanone	X	X
2-Propanone	X	
Octane		X
Heptane	X	X
1-Hexene		X
1-Heptene		X
2-Heptene		
1-Octene		X
2-Octene		
1-Pentane		X
Hexane		X
2,3,3-Trimethyl pentane		
2,3-Dimethyl hexane		
3-Methylene-heptane		
2,3,5-Trimethyl hexane		X
2,2,7-Trimethyl decane		X
3,3-dimethyl octane		
1-(1,1-dimethylethoxy)-2-propane		
Dimethyl disulfide		X
Carbon disulfide	X	
Toluene		X

[a] Volatile compounds affected by pH
[b] Volatile compounds affected by irradiation treatment

Table 3 lists the effects of pH treatments on the production of volatile compounds in ham. A significant increase in hexanal was observed with the high pH treatment when

compared with the control pH treatment. There was no difference in hexanal content between the low pH and high pH treatments. 3-Methyl butanal, 2-methyl butanal, 2-methyl propanal and heptane significantly increased with the high pH treatment when compared with the low and control pH treatments. The relative amounts of 2-butanone significantly increased with the high pH treatment when compared to the low pH treatment. Increasing the pH of the ham resulted in a significant reduction of 2-propanone. Carbon disulfide also decreased as the pH of the ham increased, but there was no difference between the control and the high pH treatment.

Table 3. Production of volatile compounds in ham with different pHs.

Volatile Compounds[1] (n = 5)	pH 5.82	pH 6.36	pH 6.72	S.E.M.
Hexanal	846^{ab}	722^{a}	986^{b}	62
3-Methyl butanal	429^{a}	429^{a}	625^{b}	25
2-Methyl butanal	275^{a}	251^{a}	388^{b}	21
2-Methyl propanal	175^{a}	141^{a}	283^{b}	16
2-Butanone	998^{a}	1121^{ab}	1595^{b}	100
2-Propanone	6671^{c}	4377^{b}	2997^{a}	275
Heptane	204^{a}	232^{a}	281^{b}	13
Carbon disulfide	290^{b}	98^{a}	21^{a}	39

[1]Total ion counts * 10^4

[a-c] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

Table 4 lists the effect of irradiation processing on the production of volatile compounds in ham. The relative amounts of ethanol, 3-methyl butanal, 2-butanone, and toluene increased significantly ($P<0.05$) in a dose-dependent manner. Volatile compounds not detected in the control samples but present in the irradiated samples included 2-methyl butanal, 2-methyl propanal, 1-hexene and 1-heptene. This is consistent with the results found by Houser and others (2005) who reported the presence of volatile compounds in irradiated

samples that were not detected in the control (0.0 kGy) samples. A significant ($P<0.05$) increase in the relative amount of heptanal, octane, 2,2,7-trimethyl decane and dimethyl disulfide was observed at 2.34 kGy and above compared to the control. The relative amounts of heptane, 1-octene, 1-pentane and hexane increased ($P<0.05$) with an irradiation treatment of 1.21 kGy and above. 2,3,5-trimethyl hexane increased ($P<0.05$) with an irradiation dose of 4.57 kGy. Ahn (2002) indicated that aldehydes such as 2-methyl butanal and 2-methyl propanal may be generated from amino acid side chains post irradiation. The same authors reported sulfur containing amino acid groups as a major source of sulfur-containing volatiles produced upon irradiation processing of glutathione and methionine-alanine.

Table 4. Production of volatile compounds in irradiated ham

Volatile Compounds[1] (n = 5)	0.0 kGy	1.21 kGy	2.34 kGy	4.57 kGy	S.E.M.
Ethanol	230^{a}	1175^{b}	1971^{c}	3079^{d}	113
Heptanal	166^{a}	188^{ab}	250^{c}	229^{bc}	14
3-Methyl butanal	15^{a}	338^{b}	580^{c}	1045^{d}	29
2-Methyl butanal	0^{a}	207^{b}	334^{c}	675^{d}	25
2-Methyl propanal	0^{a}	106^{b}	227^{c}	465^{d}	20
2-Butanone	350^{a}	913^{b}	1452^{c}	2236^{d}	113
Octane	993^{a}	1138^{ab}	1344^{b}	1428^{b}	96
Heptane	165^{a}	230^{b}	232^{b}	327^{c}	17
1-Hexene	0^{a}	114^{b}	200^{c}	377^{d}	17
1-Heptene	0^{a}	93^{b}	164^{c}	334^{d}	12
1-Octene	68^{a}	132^{b}	161^{b}	248^{c}	14
1-Pentane	14^{a}	156^{b}	321^{c}	716^{d}	40
Hexane	425^{a}	647^{b}	742^{bc}	948^{c}	70
2,3,5-Trimethyl hexane	25^{a}	29^{a}	21^{a}	82^{b}	13
2,2,7-Trimethyl decane	84^{a}	87^{a}	123^{ab}	146^{b}	14
Dimethyl disulfide	152^{a}	818^{a}	2792^{b}	3970^{c}	309
Toluene	117^{a}	324^{b}	506^{c}	787^{d}	29

[1]Total ion counts * 10^{4}

[a-d] Least squares means within the same row with different superscripts are significantly different ($P<0.05$).

The sensory evaluations showed that the saltiness of the ham was not affected by the pH or irradiation treatments. The sourness scores for the low pH, control pH and high pH treatments were 7.04, 1.64 and 1.66 with a standard error of the mean of 0.60, respectively. The trained panelists reported that the sourness was significantly ($P<0.05$) higher in the low pH samples compared to the control pH and the high pH samples. The irradiation treatments did not affected the saltiness or the sourness of the ham. A significant interaction ($P<0.02$) was observed between pH and irradiation treatment for flavor scores from the trained sensory panel (Table 5). The low pH/0.0 kGy ham received flavor scores significantly lower compared the control pH/0.0 kGy and the high pH/0.0 kGy hams. However, no significant differences in flavor scores were observed between the low and high pH hams when treated with irradiation.

Table 5. Flavor scores least squares means for pH*irradiation interaction

pH	0.0 kGy	2.34 kGy
6.72	7.36by	3.00abx
6.36	7.14by	4.16bx
5.82	4.16ay	2.52ax

[a-b] Least squares means within the same column with different superscripts are significantly different ($P<0.05$). [y-z] Least squares means within the same row with different superscripts are significantly different ($P<0.05$). Mean square error = 0.42.
0 = none, 15 = intense

The aroma, off-aroma and off-flavor of the ham were not significantly affected by the pH treatments. The aroma scores for the ham were significantly reduced by the irradiation treatments (Table 6). The off-aroma and off-flavor (aromas and flavors associated with irradiation) significantly increased with an irradiation dose of 2.34 kGy. Similar results have been reported in irradiated (4.5 kGy) ham (Houser and others 2003) and irradiated (2.0 kGy)

turkey ham (Zhu and others 2004). The higher ($P<0.05$) concentration of dimethyl disulfide and aldehydes detected in the irradiated ham may be responsible for the off-aromas and off-flavors reported by the sensory panel.

The consumer panel evaluated the aroma and flavor of three ham samples (Table 7). Consumers found no significant differences in the aroma and flavor of the low pH/0.0 kGy and control pH/0.0 kGy ham samples. However, the consumers included in this study reported significantly lower aroma and flavor scores for the low pH/2.34 kGy ham compared to the low pH/0.0 kGy and control pH/0.0 kGy hams.

Table 6. Effect of irradiation treatment on sensory properties of ham evaluated by a trained panel

Attribute (n = 5)	0.0 kGy	2.34 kGy	S.E.M.
Aroma	6.49^{b}	2.98^{a}	0.25
Off-aroma	1.52^{a}	6.76^{b}	0.52
Off-flavor	1.14^{a}	4.85^{b}	0.53

$^{a-b}$ Least squares means within the same row with different superscripts are significantly different ($P<0.05$).
0 = none, 15 = intense

Table 7. Effect of pH and irradiation treatment on aroma and flavor scores of ham evaluated by a consumer panel

Treatment	Aroma (n = 5)	Flavor (n = 5)
pH 6.36/0.0 kGy	5.72^{b}	6.30^{b}
pH 5.82/0.0 kGy	5.67^{b}	6.22^{b}
pH 5.82/2.34 kGy	4.37^{a}	5.12^{a}
S.E.M.	0.25	0.18

$^{a-b}$ Least squares means within the same row with different superscripts are significantly different ($P<0.05$).
0 = none, 15 = intense

Conclusion

The pH treatments altered the production of volatile compounds in ham including a lipid oxidation product (hexanal) and a sulfur-containing compound (carbon disulfide). However, the aroma of the ham was not affected by the pH treatments. The major impact on the production of volatile compounds was caused by the irradiation treatments. The trained sensory panel indicated that the aroma associated with ham was significantly decreased by irradiation processing. The consumer panel confirmed these results giving the irradiated sample lower scores for aroma and flavor. The lower scores for the aroma and flavor of the irradiated ham reported by the sensory panels could be attributed to the higher concentration of sulfur-containing compounds in this sample.

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CHAPTER 6. GENERAL CONCLUSIONS

A significant increase in CIE a* values for turkey rolls was the only effect of irradiation processing on the color of the RTE products included in these studies. On the other hand, irradiation processing resulted in significant changes in quality characteristics such as odor/aroma, and flavor of most of the products studied. Furthermore, the production of volatile compounds was altered by the irradiation treatments in most cases regardless of animal species. Trained and consumer panels found significant differences in the quality characteristics of the irradiated product evaluated.

The pH treatments altered the production of volatile compounds in ham including a lipid oxidation product (hexanal) and a sulfur-containing compound (carbon disulfide). However, the major impact on the production of volatile compounds was caused by the irradiation treatments. The production of volatiles increased as a result of irradiation treatment for most compounds including sulfur-containing compounds. Volatile compounds such as 2-methyl butanal, 2-methyl propanal, 1-hexene, 1-heptene were not detected in the control samples but were present in the irradiated samples. The irradiated beef frankfurters was the only product tested that showed decreased levels of dimethyl disulfide as a result of irradiation processing. The volatiles from some of the spices used in the formulation of the beef frankfurters increased as a result of irradiation processing.

Irradiation processing affected the typical odor/aroma characteristics of ham, corned beef, roast beef, chicken roll, cured turkey roll and turkey frankfurters. Irradiation also changed the flavor properties of the ham, cured turkey roll and pork frankfurters. A significant interaction was observed between pH and irradiation treatment for flavor scores of ham from the trained sensory panel. The low pH/0.0 kGy ham received flavor scores

significantly lower compared the control pH/0.0 kGy and the high pH/0.0 kGy hams. However, no significant differences in flavor scores were observed between the low and high pH hams when the product was treated with irradiation. In addition, the consumers included in this study reported significantly lower aroma and flavor scores for the irradiated samples when compared with its non-irradiated counterparts.

This research is intended to provide baseline to approach many questions that remain unanswered regarding the impact of irradiation processing on the quality characteristics of RTE meats. Irradiation processing affected the quality characteristics of most of the products tested in these studies. It is evident that the changes in odor/aroma and flavor of the RTE products included in these studies were negatively impacted by irradiation processing. The significant increase in volatile compounds such as sulfur-containing compounds could be responsible for the quality changes detected by the panelists. The consumer test performed with the irradiated ham provides evidence that more research is needed to find ways to minimize the changes in the quality characteristics of this product.

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